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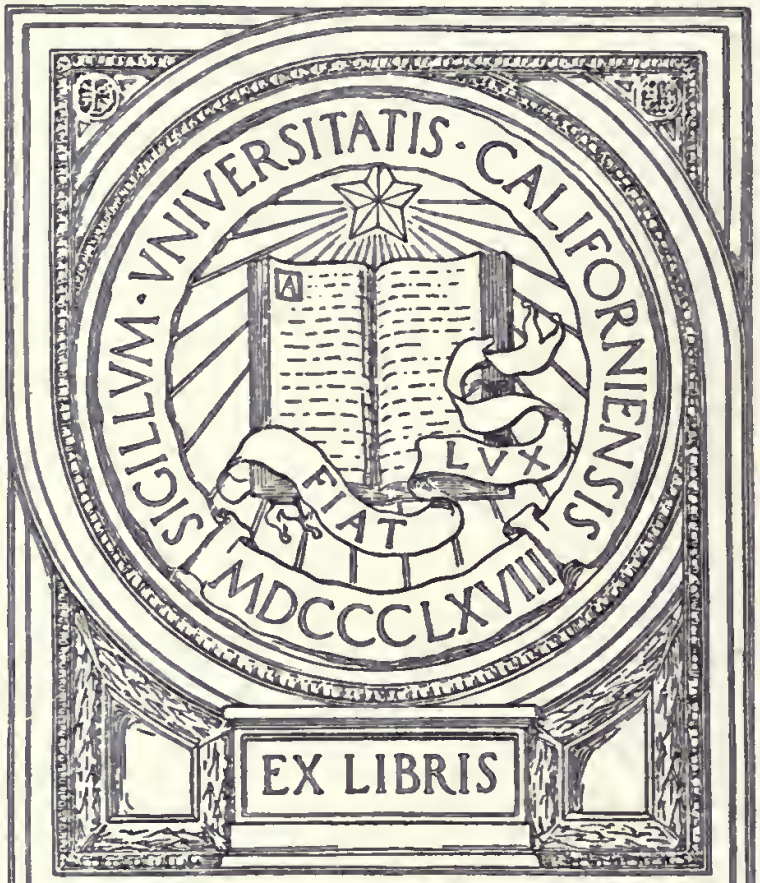

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KINETIC THEORY OF GASES

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Clarendon Press Series

A TREATISE

ON THE

KINETIC THEORY OF GASES

BY

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FORMERLY FELLOW OF TRINITY COLLEGE, CAMBRIDGE

SECOND EDITION

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PREFACE TO FIRST EDITION

THE idea of a Kinetic Theory of Gases originated with J. Bernouilli about the middle of the last century, but the first establishment of the theory on a scientific basis is due to Professor Clausius.

During the last few years the theory has been greatly developed by many physicists, especially by Professor Clerk Maxwell in England and Professor Clausius and Dr. Ludwig Boltzmann on the Continent; and although still beset by formidable difficulties, it has succeeded in explaining most of the established laws of gases in so remarkable a manner as to render it well worthy of the attentive consideration of scientific men.

My object in the following short treatise is to make the existing state of the theory more widely known by presenting some of the scattered memoirs of the writers I have mentioned in a systematic and continuous form, in the hope that mathematicians may be induced to turn their attention to the theory, and thus assist in removing, if possible, the obstacles which yet remain in the way of its complete establishment.

For the most part I have followed the method of treatment adopted by Dr. Ludwig Boltzmann in some very interesting memoirs contributed by him to the

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Transactions of the Imperial Academy of Vienna,* but in some cases I have varied this treatment for the sake of greater conciseness or greater generality.

Thus, in place of Dr. L. Boltzmann's conception of a molecule as a collection of mutually attracting particles, I have substituted the more general conception of a material system possessing a given number of degrees of freedom, that is to say, a given number of generalised coordinates.

Again, in the deduction of the second law of Thermodynamics from the results of the Kinetic Theory, I felt some difficulty in following Dr. Boltzmann's reasoning, and I originally proposed to substitute for it a demonstration of my own, free from what appeared to me to be the obscurities of Dr. Boltzmann's reasoning, but applicable only to the case in which there were no intermolecular actions. My friend Mr. S. H. Burbury, formerly Fellow of St. John's College, Cambridge, to whom I communicated my difficulties, has invented an unexceptionable proof applicable to all cases, which he published last January in the London, Edinburgh, and Dublin Philosophical Magazine, and with his permission I have adopted this proof in the following treatise.

To Professor Clerk Maxwell I am indebted for much kind assistance, and especially for access to some of his manuscript notes on this subject, from which I have taken many valuable suggestions.

H. W. WATSON.

BERKSWELL RECTORY, COVENTRY:
Sept. 17, 1876.

* Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften Wien, Band 63, 1871, und Band 66, 1872.

PREFACE TO SECOND EDITION

MUCH interest has been manifested by physicists during the last thirty years in the Kinetic Theory of Gases.

This interest has been greatly stimulated by the researches of Maxwell in England and Boltzmann in Germany; but along with a growing conviction of the truth of *a* Kinetic Theory in its general aspect, the particular conclusions arrived at by these investigators concerning the laws of permanent distribution have been received with great distrust; they have been subjected to hostile criticism from mathematicians of such eminence that the mere weight of their authority must almost be accepted as conclusive, were there not room for the contention that these criticisms are not really directed against the laws themselves, as stated and applied in the Kinetic Theory, but against certain aspects of those laws with which the theory is not concerned.

The object of the original edition of this book was, as stated in the preface thereto, to set forth in a more systematic, and in some cases a more simple form, the

demonstrations of these laws contained chiefly in the Transactions of the Royal Society of London, the Imperial Academy of Vienna, and sundry papers in the Philosophical Magazine and other scientific journals. Boltzmann's methods, especially, were closely followed, with occasional modifications, the most important of these being the substitution, in the conception of a molecule, of a material system with a determinate number of degrees of freedom, for a determinate number of discrete atoms under the action of mutual forces. In the present edition the ground covered is substantially the same as in the original edition, and is limited, as it was in that case, to the investigation of the laws of permanent distribution, but in much greater detail; so much so, indeed, as to be liable to the charge of undue prolixity, inasmuch as there is spread over several propositions of increasing generality that which might really have been condensed into the single proposition of Art. 14. This more detailed treatment, however, has been deliberately adopted, partly because there is an historical interest in retaining the steps by which the theory has actually been developed, but mainly to avoid the extreme difficulty on the part of the student in following out investigations of the great generality required in the single proposition treatment. Even to the minds of advanced mathematicians the vagueness imparted to the reasoning by the more condensed treatment has been suggestive of inconclusiveness, while to the learner it presents almost insuperable obstacles. The more detailed treatment, with its continual repetitions, has the advantage of investing each step of the process with a

distinct mechanical meaning, rendering the demonstration easier to follow and more convincing when mastered. The one essential condition is that the statistical treatment should be always kept in view, the slightest attempt to impart direction or control being fatal.

The investigations of the following pages appear to point strongly to the conclusion that in a medium consisting of sets of a very large number of similar constituents, called molecules, each molecule being a material system with a definite number of degrees of freedom, and all being in irregular and undirected motion, and in a field of fixed central forces only, that is, free from finite distance intermolecular forces, the physical properties of the medium will be in entire accordance with the accepted laws of ideal perfect gases, provided only that either the molecular density of the medium or the minimum irreducible volume of each molecule be so small that the total molecular volume per unit of volume is a small fraction.

Should there be appreciable finite distance intermolecular forces, it is obvious that in one respect the agreement in physical properties of the medium and the ideal perfect gas cannot be maintained, because there must be work done in the former by compression or expansion, but even in such a case (see Art. 21) the accordance may remain in the five particulars enumerated in Art. 23. And under any circumstances it is true that the rarer the medium the more nearly do its properties correspond with those of the ideal gas, exactly as we find to be the case in the gases of ordinary experience.

In conclusion, I desire to acknowledge the valuable help

most kindly afforded me by friends in the preparation of this Edition, among whom I would especially mention Mr. S. H. Burbury, M.A., F.R.S., formerly Fellow of St. John's College, Cambridge, and Mr. G. H. Bryan, M.A., Fellow of St. Peter's College, Cambridge.

H. W. WATSON.

Berkswell Rectory, Coventry,
June, 1893.

INTRODUCTION

THE Kinetic Theory of Gases is based upon the conception of an infinitely large number of molecules in motion in a given space with velocities of all degrees of intensity and in all conceivable directions. These molecules, as will be explained in the course of the following treatise, may sometimes be regarded as smooth spheres, in which case we shall only have to consider the motion of translation of the centre of mass of each of them, or they may be regarded as bodies of any form capable of any number of internal vibrations. It is clear that the individual molecules in such a system must be continually acting upon each other, either in the way of collision, like the mutual impacts of elastic spheres, or else in the more gradual way of mutual attraction and repulsion ; such actions are called encounters.

It is easy to see that if encounters take place among a great number of molecules, their velocities, even if originally equal, will become unequal, for, except under conditions which can be only rarely satisfied, two molecules having equal velocities before their encounter will have unequal velocities after such encounter. Now, as long as we have to deal with only two molecules, and have all the

data of an encounter given us, we can calculate the result of their mutual action; but when we have to deal with millions of molecules, each of which has millions of encounters in a second, the complexity of the problem seems to shut out all hope of a legitimate solution.

We are obliged therefore to abandon the strictly kinetic method and to adopt the statistical method.

According to the strict kinetic or historical method as applied to the case before us, we follow the whole course of every individual molecule. We arrange our symbols so as to be able to identify every molecule throughout its motion, and the complete solution of the problem would enable us to determine at any given instant the position and motion of any given molecule from a knowledge of the positions and motions of all the molecules in their initial state.

According to the statistical method, the state of the system at any instant is ascertained by distributing the molecules into groups, the definition of each group being founded on some variable property of the molecules. Each individual molecule is sometimes in one of these groups and sometimes in another, but we make no attempt to follow it; we simply take account of the number of molecules which at a given instant belong to each group.

Thus we may consider as a group those molecules which at a given instant lie within a given region of space. Molecules may pass into or out of this region, but we confine our attention to the increase or diminution of the number of molecules within it. Just as the population of a watering-place, considered as a mere number, varies in the same way whether its visitors return to it season after season, or whether the annual gathering consists each year of fresh individuals. Or we may form our group out of

those molecules which at a given instant have velocities lying within given limits. When a molecule has an encounter and changes its velocity, it passes out of one of these groups and enters another; but as other molecules are also changing their velocities, the number of molecules in each group varies little from a certain average value.

We thus meet with a new kind of regularity, the regularity of averages, a regularity which, when we are dealing with millions of millions of individuals, is so unvarying that we are almost in danger of confounding it with absolute uniformity.

Laplace, in his Theory of Probability, has given many examples of this kind of statistical regularity, and has shown how this regularity is consistent with the utmost irregularity among the individual instances which are enumerated in making up the results.*

These observations must be borne in mind in interpreting the definitions laid down and the results arrived at in the Kinetic Theory of Gases.

Thus, to refer to the illustrations already given, we shall prove that the number of molecules lying within a certain region of space, or the number of molecules having their velocities within certain limits differing by some finite quantity, is in each case a number bearing some finite ratio to the total number of molecules in the mass under consideration, and therefore infinitely large. But these results are to be interpreted as average results. We do not assert by them, nor are we capable of proving, that at any given instant there is one single molecule satisfying either of the required conditions, that is, comprised within either of the contemplated groups.

* MS. notes by Professor Clerk Maxwell.

So, again, the density of the region in the neighbourhood of any point is defined as the limit of the quotient of the number representing the aggregate masses of the molecules within any volume containing the point, to the number representing that volume, when the volume is indefinitely diminished. In interpreting this definition two things must be remembered. In the first place, according to what has been said just now, we do not assert and cannot prove that there is, as a matter of fact, any particular number of molecules within the volume containing the given point, at any given instant; and in the second place, supposing we could prove that the number of molecules within the volume was thus accurately determined, yet even so there could be no point within the region at which the actual density of the matter had the value determined by our definition; for if the point were within a molecule the actual density would be much greater, and if it were not within a molecule the density would be zero.

KINETIC THEORY OF GASES

ART. 1.] A very great number of smooth elastic spheres, equal in every respect, are in motion within a region of space of given volume, and therefore occasionally impinge upon each other with various degrees of relative velocity and in various directions. The space is so large in proportion to the sum of the volumes of the spheres that the average time during which any one sphere is moving free from contact with any other is infinitely greater than the average time during which it is in collision with some other sphere*. Required to find the law according to which the velocities must be distributed in order that such distribution may be permanent.

Let N be the total number of spheres, and let

$$\chi(u, v, w)\, du\, dv\, dw$$

be the number of spheres whose component velocities parallel to the axes are intermediate between

$$u \text{ and } u+du, \quad v \text{ and } v+dv, \quad w \text{ and } w+dw$$

respectively.

* In the mathematical conception of a collision as an absolutely instantaneous phenomenon the proviso in the text is of course superfluous. An actual physical collision must take some time, however short, and the object of the proviso is to exclude the possibility, or rather to diminish indefinitely the probability, of the occurrence of cases in which the collision of one sphere with a second is not concluded before that with a third commences.

If we change the variables and make c the resultant velocity, θ the inclination of c to the axis of z, and ϕ that of the plane of cz to the plane of xz, the expression given above will become

$$\chi(u, v, w)\, c^2 \sin\theta\, d\theta\, d\phi\, dc.$$

Let a spherical surface of radius unity be described round the origin as centre, and let us write $d\sigma$ for the element $\sin\theta\, d\theta\, d\phi$ on this spherical surface, then the last written expression becomes

$$\chi(u, v, w)\, c^2 dc\, d\sigma.$$

Since for the same magnitude of the resultant velocity all directions must be equally probable, it follows that the coefficient of $dc\, d\sigma$ in this expression must be a function of the resultant velocity c only, and therefore the number of spheres having component velocities between u and $u+du$, v and $v+dv$, w and $w+dw$ must be

$$\psi(c)\, du\, dv\, dw.$$

It is required, now, to find the form of ψ in order that the value of this expression may be unaffected by collisions.

We assume that in the permanent state the distribution of the spheres throughout the space occupied by them is homogeneous in all respects; that is to say, on an average of any long time there are the same number of spheres in a given volume wherever that volume may be situated, and the law of distribution of velocities is the same throughout that volume as in the whole region under consideration.

Hence the number of pairs of spheres having component velocities between

$$u_1 \text{ and } u_1+du_1, \quad v_1 \text{ and } v_1+dv_1, \quad w_1 \text{ and } w_1+dw_1$$

for the one, and

u_2 and u_2+du_2, v_2 and v_2+dv_2, w_2 and w_2+dw_2

for the other, and such that the lengths of the projections of their line of centres upon the axes are between

$$x \text{ and } x+dx, \quad y \text{ and } y+dy, \quad z \text{ and } z+dz,$$

must be proportional to

$$\psi(c_1)\,\psi(c_2)\,du_1 dv_1 dw_1 du_2 dv_2 dw_2 dx dy dz, \quad . \quad . \quad \text{(A)}$$

where c_1 and c_2 are the resultant velocities.

Since the coefficient of $dxdydz$ is independent of x, y, z, it follows that the number of pairs having their velocities between the above-mentioned limits and the projections of their line of centres between x and $x+dx$, 0 and dy, 0 and dz must be also represented by (A).

If dy and dz be infinitesimal in comparison with the diameter of any sphere, the lines of centres are parallel to the axis of x and the velocity of approach of these centres is u_1-u_2.

If d be the sum of the radii of any two of the spheres, or, what is the same thing in this case, the diameter of any one of them, then it follows that any pair of spheres having the x component of their line of centres less than $d+(u_1-u_2)\,dt$ will encounter each other in the time dt; making therefore

$$x = d \text{ and } dx = (u_1-u_2)\,dt,$$

it will follow that the number of collisions in time dt of pairs of spheres with their lines of centres parallel to x and velocities between the above limits is proportional to

$$\psi(c_1)\,\psi(c_2)\,du_1 \ldots dw_2 dy\,dz\,(u_1-u_2)\,dt. \quad . \quad . \quad \text{(B)}$$

After collision let the different quantities involved in (B) become c_1', c_2', u_1', &c., while x, y, and z, dy and dz remain of course unchanged.

It follows therefore that if the values of these velocities and component velocities had originally been within the limits indicated by the accented letters with reversed signs, the spheres would, after collision, have passed into the original state as indicated by the unaccented letters. Call these states E and F respectively. For permanence of distribution therefore it is sufficient that the number of collisions of pairs of spheres in state E during the time dt should be equal to the number of collisions of pairs in the state F during the same time; and therefore that

$$\psi(c_1)\,\psi(c_2)\,du_1 \ldots dw_2\,dy\,dz\,(u_1-u_2) = \psi(c_1')\,\psi(c_2')\,du_1' \ldots dw_2'\,dy\,dz\,(u_2'-u_1').$$

Now

$$\begin{aligned} u_1' &= u_2, & \therefore\ du_1' &= du_2,\\ u_2' &= u_1, & du_2' &= du_1,\\ v_1 &= v_1', & dv_1 &= dv_1',\\ v_2 &= v_2', & dv_2 &= dv_2',\\ w &= w_1', & dw_1 &= dw_1',\\ w_2 &= w_2', & dw_2 &= dw_2'. \end{aligned}$$

Hence

$$du_1 \ldots dw_2\,dy\,dz\,(u_1-u_2) = du_1' \ldots dw_2'\,dy\,dz\,(u_2'-u_1');$$

$$\therefore\ \psi(c_1)\,\psi(c_2) = \psi(c_1')\,\psi(c_2'),$$

and

$$c_1^2 + c_2^2 = c_1'^2 + c_2'^2.$$

This functional equation may be integrated as follows. Let it be expressed in the form

$$\chi(c_1^2)\,\chi(c_2^2) = \chi(c_1'^2)\,\chi(c_2'^2),$$

and for c_1^2 and c_2^2 write x and x', and for $c_1'^2$ and $c_2'^2$ write y and y'; then we have

$$\chi(x)\,\chi(x') = \chi(y)\,\chi(y'),$$

where

$$x + x' = y + y';$$

$$\therefore\ \chi(x)\chi(x') = \chi(y)\chi(x+x'-y);$$

therefore differentiating with respect to x and x',

$$\chi'(x)\chi(x') = \chi(y)\chi'(x+x'-y);$$

and

$$\chi(x)\chi'(x') = \chi(y)\chi'(x+x'-y);$$

$$\therefore\ \frac{\chi'(x)}{\chi(x)} = \frac{\chi'(x')}{\chi(x')};$$

that is,

$$\frac{\chi'(x)}{\chi(x)} = \text{constant};$$

$$\therefore\ \chi(x) = Ae^{-hx};$$ and why is it $-h$?

$$\therefore\ \psi(c) = Ae^{-hc^2}.$$

Now the axis of x may be taken in any direction. Whence it follows that this form of ψ will ensure the permanence of distribution for all possible collisions.

Therefore the number of spheres with component velocities between u and $u+du$, v and $v+dv$, w and $w+dw$

is

$$Ae^{-hc^2}\,du\,dv\,dw,$$

or

$$Ae^{-hc^2}c^2\,dc\,d\sigma,$$

employing the notation used above.

Integrating with respect to $d\sigma$ from 0 to 4π, we find for the number of spheres with velocities between c and $c+dc$ the expression

$$4\pi\,Ae^{-hc^2}c^2\,dc.$$

Again, since the number with component velocities between

u and $u+du$, v and $v+dv$, w and $w+dw$

is

$$Ae^{-h(u^2+v^2+w^2)}\,du\,dv\,dw,$$

or

$$\sqrt[3]{Ae^{-hu^2}}\,du\,\sqrt[3]{Ae^{-hv^2}}\,dv\,\sqrt[3]{Ae^{-hw^2}}\,dw,$$

it follows that the number of spheres having velocities intermediate between u and $u+du$ parallel to any fixed line is

$$Ae^{-hu^2}\,du\int_{-\infty}^{\infty}e^{-hv^2}\,dv\int_{-\infty}^{\infty}e^{-hw^2}\,dw;$$

that is

$$Ae^{-hu^2}\,du\,\frac{\pi}{h};$$

where A may be determined by the equation

$$A\frac{\pi}{h}\int_{-\infty}^{\infty}e^{-hu^2}\,du=N;$$

or

$$A\frac{\pi^{\frac{3}{2}}}{h^{\frac{3}{2}}}=N;$$

and therefore

$$A=\frac{Nh^{\frac{3}{2}}}{\pi^{\frac{3}{2}}},$$

that is to say, the number of spheres having velocities between c and $c+dc$ is

$$\frac{4Nh^{\frac{3}{2}}}{\sqrt{\pi}}.\,e^{-hc^2}c^2\,dc.$$

If we multiply this expression by c, integrate the product with regard to c from 0 to ∞ and divide by N, we find the mean velocity of all the spheres to be

$$\frac{2}{\sqrt{\pi}h}.$$

And, similarly, multiplying by c^2 instead of c, we find the mean square of the velocities to be

$$\frac{3}{2h},$$

and this is greater than the square of the mean velocity, as it ought to be.

2.] Before we proceed further it will be useful to make a formal statement of the method employed in the last Article for denoting the velocities of particles or material points.

Instead of drawing straight lines from each particle indicating the magnitude and direction of the velocity of that particle, we draw all such straight lines for all particles from any assumed point taken as the origin.

This method is very useful when, as in investigations like the present, we wish to compare the simultaneous velocities of different particles as well as the successive velocities of each particle separately.

We thus obtain a figure every point of which corresponds to one of our particles, the velocity of that particle is represented in magnitude and direction by a line drawn from the origin to the corresponding point, and the relative velocity of any two particles is also represented by the line joining the points corresponding to these two particles. If the system have a common velocity, then we must suppose the position of the new origin of the diagram of velocities with respect to the old origin to be so chosen as to represent this velocity.

In studying the motion of the system it is found convenient to divide the particles into groups according to their velocities, those particles whose velocities lie within certain limits with respect to magnitude and direction being placed in the same group.

In the velocity diagram these particles are indicated at once by the points which correspond to them being included within a certain small region or elementary volume of the diagram, the boundary of this region corresponding to the given limits of velocity.

Thus, in the proposition just now considered, the state E might be described as that in which the velocity points

are situated within the elementary volume

$$du\,dv\,dw \quad \text{or} \quad c^2 \sin\theta\, d\theta\, \delta\phi\, dc$$

of the diagram of velocities.

We may also conveniently make use of the term velocity-density to indicate the result of dividing the number of particles whose velocities lie within the given limits by the volume of the corresponding region in the diagram of velocities.

3.] Let the N elastic spheres of the last Article be replaced by two sets, one of N spheres each having mass m, and the other of N' spheres each having mass m', and let us find the law of distribution of the velocities of the N and N' spheres respectively.

Exactly as in the first Article, it may be proved that the number of the N spheres whose component velocities parallel to the axes are intermediate between

$$u \text{ and } u+du, \quad v \text{ and } v+dv, \quad w \text{ and } w+dw$$

respectively must be

$$\psi(c)\,du\,dv\,dw,$$

where

$$c^2 = u^2+v^2+w^2;$$

and that the number of the N' spheres whose component velocities are intermediate between

$$u' \text{ and } u'+du', \quad v' \text{ and } v'+dv', \quad w' \text{ and } w'+dw'$$

must be

$$\psi_1(c')\,du'\,dv'\,dw';$$

and that the number of collisions in time dt between pairs of spheres, one from each set, with lines of centres parallel to the axis of x and component velocities between the above limits respectively, must be proportional to

$$\psi(c)\,\psi_1(c')\,du\,dv\,dw\,du'\,dv'\,dw'\,(u-u')\,dt. \quad . \quad . \quad (A)$$

If the component velocities of these spheres after collision be between

$$U \text{ and } U+dU, \quad V \text{ and } V+dV, \quad W \text{ and } W+dW,$$

$$U' \text{ and } U'+dU', \quad V' \text{ and } V'+dV', \quad W' \text{ and } W'+dW'$$

respectively, then, by the reasoning employed in the last case, we must have

$$\psi(c)\,\psi_1(c')\,du \ldots dw'\,(u-u') = \psi(C)\,\psi_1(C')\,dU \ldots dW'\,(U'-U), \quad . \quad \text{(B)}$$

where $V=v, \quad W=w, \quad V'=v', \quad W'=w',$

$$U = u - \frac{2m'}{m+m'}(u-u'),$$

$$U' = u' + \frac{2m}{m+m'}(u-u');$$

whence we get $mC^2+m'C'^2 = mc^2+m'c'^2,$

$$\frac{dU}{du'}\frac{dU'}{du} - \frac{dU}{du}\cdot\frac{dU'}{du'} = \frac{(m-m')^2}{(m+m')^2} + \frac{4mm'}{(m+m')^2} = 1;$$

and also

$$dV=dv, \quad dW=dw, \quad dV'=dv', \quad dW=dw',$$

$$U'-U = u-u',$$

and $$dU\,dU' = du\,du'\left(\frac{dU}{du'}\frac{dU'}{du} - \frac{dU}{du}\frac{dU'}{du'}\right) = du\,du'.$$

So that equation (B) reduces to

$$\psi(c)\,\psi_1(c') = \psi(C)\,\psi_1(C'),$$

where $$mc^2+m'c'^2 = mC^2+m'C'^2.$$

A functional equation of which, as before, the solution may be shewn to be

$$\psi(c) = Ae^{-h\frac{mc^2}{2}} \quad \text{and} \quad \psi_1(c') = Be^{-h\frac{m'c'^2}{2}}.$$

It must be remembered that h is here a constant of different dimensions from the h of the former case.

Since the axis of x may be taken in any direction, it follows that these forms of ψ and ψ_1 will ensure the permanence of distribution as far as collisions between spheres of two different sets are concerned, and we have already proved that they will ensure that permanence so far as collisions between spheres of the same set are concerned; therefore it follows that the number of the N spheres whose component velocities are intermediate between

$$u \text{ and } u+du, \quad v \text{ and } v+dv, \quad w \text{ and } w+dw$$

must be $$Ae^{-h\frac{mc^2}{2}}du\,dv\,dw,$$

where $$c^2 = u^2+v^2+w^2;$$

and the number of the N' spheres whose component velocities are intermediate between

$$u' \text{ and } u'+du', \quad v' \text{ and } v'+dv', \quad w' \text{ and } w'+dw'$$

must be $$Be^{-h\frac{m'c'^2}{2}}du'\,dv'\,dw',$$

where $$c'^2 = u'^2+v'^2+w'^2;$$

and it is clear that the same reasoning would hold whatever number of sets of such spheres the space might contain.

Applying the results of the former case, and writing

$$\frac{mh}{2}, \frac{m'h}{2}$$

instead of h, we get

$$A = \frac{N}{\pi^{\frac{3}{2}}}\cdot\left(\frac{mh}{2}\right)^{\frac{3}{2}}, \quad B = \frac{N'}{\pi^{\frac{3}{2}}}\cdot\left(\frac{m'h}{2}\right)^{\frac{3}{2}};$$

and so on for any other sets which the region may contain.

We also find that the mean velocity of each of the N spheres is

$$\frac{2}{\sqrt{\pi}} \cdot \sqrt{\frac{2}{mh}},$$

and similarly for the remaining sets of spheres.

Also the mean square of the velocity of each of the N spheres is

$$\frac{3}{2} \cdot \frac{2}{mh},$$

and the mean kinetic energy

$$\frac{3}{2h},$$

the last result being the same for each set of spheres.

4.] On the hypothesis of the last Article to find the number of pairs of spheres, one being taken from the N set and the other from the N' set, whose relative velocities lie between given limits, and the number of collisions in unit of time and unit of volume between these sets of spheres.

Using the results of the last Article, writing $\frac{1}{\alpha^2}$ for $\frac{hm}{2}$ and $\frac{1}{\beta^2}$ for $\frac{hm'}{2}$, and supposing the volume of the region considered to be the unit of volume, we find that the number of spheres of the N set which have their component velocities parallel to x between the limits u and $u + du$ is

$$\frac{N}{\alpha\sqrt{\pi}} \cdot e^{-\frac{u^2}{\alpha^2}} du; \quad \ldots\ldots \quad \text{(A)}$$

and that the number of spheres of the N' set which have their component velocities parallel to x between the limits $u + U$ and $u + U + dU$ is

$$\frac{N'}{\beta\sqrt{\pi}} \cdot e^{-\frac{(u+U)^2}{\beta^2}} dU; \quad \ldots\ldots \quad \text{(B)}$$

and therefore the number of pairs of spheres fulfilling the above-mentioned conditions is

$$\frac{NN'}{\alpha\beta\pi} \cdot e^{-\left\{\frac{u^2}{\alpha^2}+\frac{(u+U)^2}{\beta^2}\right\}} du\, dU.$$

Integrating with respect to u from $-\infty$ to $+\infty$, we find for the total number of pairs of spheres whose relative velocity parallel to x lies between U and $U+dU$, the expression

$$\frac{NN'}{\sqrt{\alpha^2+\beta^2}} \cdot \frac{1}{\sqrt{\pi}} e^{-\frac{U^2}{\alpha^2+\beta^2}} dU. \quad . \quad . \quad . \quad . \quad (C)$$

Comparing (C) with (A) we see that the distribution of relative velocities follows a law of the same form as that of absolute velocities, and therefore that the mean relative velocity is the square root of the sum of the squares of the mean absolute velocities in the two systems, and the mean square of the relative velocity is the sum of the mean squares of the absolute velocities.

It follows also of course that the number of pairs of spheres, one from each set, whose relative velocities lie between r and $r+dr$ is

$$NN' \frac{4}{\sqrt{\pi}\,(\alpha^2+\beta^2)^{\frac{3}{2}}} \cdot e^{-\frac{r^2}{\alpha^2+\beta^2}} r^2\, dr\,;$$

or, restoring to α and β their values,

$$NN' \frac{\sqrt{2}}{\sqrt{\pi}} \cdot \frac{(mm'h)^{\frac{3}{2}}}{(m+m')^{\frac{3}{2}}} \cdot e^{-\frac{r^2 mm' h}{2(m+m')}} r^2\, dr.$$

5.] We proceed now to find the number of collisions in unit of time and volume between the spheres of the N set and those of the N' set.

Suppose a number N of equal spheres at rest to be distributed in any manner throughout a unit of volume,

and suppose that another sphere moves among them with the velocity r. If a tubular surface be described having for axis the path of the centre of this moving sphere, and for its radius s, or the sum of the radii of the moving sphere and one of the stationary spheres, the volume of the surface thus generated in a unit of time by the moving sphere will be $\pi r s^2$. Hence the chance of the moving sphere colliding with any one of the fixed spheres in a unit of time must be $\pi r s^2$, and the number of collisions in unit of time between the moving sphere and stationary spheres must be $N \pi r s^2$.

The same results would hold good if we replaced the stationary spheres by spheres moving with a common velocity and the moving sphere had a velocity r relative to each of them, that is to say, the chance of collision in unit of time between the last-mentioned sphere and any one of the former-mentioned spheres would be $\pi r s^2$.

Suppose now that there are two sets of N and N' spheres in the unit of volume, and that the number of pairs of spheres (one being taken from each set) whose relative velocities are between r and $r + dr$ is nn', then, if s be the sum of the radii of each pair, it will follow that the chance of a collision between any pair in unit of time is $\pi r s^2$, and therefore that the total number of collisions in unit of volume and unit of time is $nn' \pi r s^2$.

But we have already seen that nn' is equal to

$$NN' \frac{4}{\sqrt{\pi}\,(\alpha^2+\beta^2)^{\frac{3}{2}}} e^{-\frac{r^2}{\alpha^2+\beta^2}} r^2 \, dr,$$

N and N' being the total number of spheres of each set in unit-volume, and α^2 and β^2 being written for $\frac{2}{mh}$ and $\frac{2}{m'h}$, as before.

Hence the number of collisions in unit-time between

pairs of spheres whose relative velocity lies between r and $r+dr$ is

$$NN' \frac{4\sqrt{\pi}}{(\alpha^2+\beta^2)^{\frac{3}{2}}} \cdot s^2 r^3 e^{-\frac{r^2}{\alpha^2+\beta^2}} dr;$$

or

$$NN' \sqrt{2\pi} \cdot \frac{(mm'h)^{\frac{3}{2}}}{(m+m')^{\frac{3}{2}}} \cdot s^2 r^3 e^{-\frac{r^2 mm' h}{2(m+m')}} dr.$$

Integrating from $r = 0$ to $r = \infty$, we get

$$2NN' \sqrt{\pi} \cdot \sqrt{\alpha^2+\beta^2}\, s^2$$

or

$$2NN \sqrt{\pi} \sqrt{\frac{2(m+m')}{mm'h}} \cdot s^2$$

for the number of collisions in unit of time which take place in unit of volume between spheres of the N and N' sets.

The number of collisions in the same time and volume between spheres of the N set is therefore

$$2N^2 \sqrt{\pi} \sqrt{2\alpha^2} \cdot s_1^2,$$

or

$$\frac{4N^2\sqrt{\pi}}{\sqrt{mh}} \cdot s_1^2;$$

and between spheres of the N' set the number is

$$2N'^2 \sqrt{\pi} \sqrt{2\beta^2}\, s_2^2,$$

or

$$\frac{4N'^2\sqrt{\pi}}{\sqrt{m'h}} \cdot s_2^2.$$

Also, since the mean velocities in the two systems are

$$\frac{2\alpha}{\sqrt{\pi}} \text{ and } \frac{2\beta}{\sqrt{\pi}},$$

it follows that if l_1 be the mean distance travelled by a sphere of the N_1 set between each collision with a sphere

of its own set and l_2 the corresponding mean distance for the second set, then

$$\frac{1}{l_1} = \pi N_1 \sqrt{2}\, s_1^2 \quad \text{and} \quad \frac{1}{l_1} = \pi N_2 \sqrt{2}\, s_2^2,$$

s_1 and s_2 being diameters of spheres of the two sets.

Also, if λ_1 be the mean distance travelled by a sphere of the N_1 set without any collision whatever,

$$\frac{1}{\lambda_1} = \pi N_1 \sqrt{2}\, s_1^2 + \pi N_2 \frac{\sqrt{a^2+\beta^2}}{a} {}_1s_2^2 + \pi N_3 \frac{\sqrt{a^2+\gamma^2}}{a} {}_1s_3^2 + \&c.;$$

where ${}_1s_r$ is sum of radii of spheres of the N_1 and N_r sets, with a similar expression for the mean distance travelled by a sphere of any other set.

6.] Let the sets of spheres of the previous cases be replaced by sets of perfectly smooth and elastic circular disks with their centres of inertia not coincident with their centres of figure, in motion within a plane area inclosed by a perfectly elastic boundary, the number of disks in each set being very great. The disks in each set are equal to each other in every respect, while those in different sets may differ in mass, area, and distance between the centre of inertia and the centre of figure.

Each disk has in this case three degrees of freedom, which may be expressed by the coordinates of the centre of figure and the angle between the line joining the centres of figure and inertia, and some fixed line, as the axis of x; or perhaps more conveniently by the perpendicular distance of the centre of inertia from a line through that of figure parallel to the x axis. There are three corresponding momenta components measured, for each disk, by the translational x and y velocities u and v of the centre of inertia, and the angular velocity ω round an axis perpen-

dicular to the disk. In this case it is clear that any assumed distribution of momenta for the disks of each set will, in the absence of all collisions, remain undisturbed, it is required to investigate the conditions of such permanence when there are collisions between two disks of the same or different sets.

Let the expression

$$f_1(u, v, \omega)\, du\, dv\, d\omega$$

represent the number of the disks of any set with velocity-components intermediate between u, $u+du$; v, $v+dv$; ω, $\omega+d\omega$; and let

$$f_2(U, V, \Omega)\, dU\, dV\, d\Omega$$

be a corresponding expression for any other set; and let us consider the effect of collisions, one at a time, between disks of these two sets.

The number of pairs of such disks with velocity-components, at any instant, between the aforesaid limits is

$$f_1(u, v, \omega) f_2(U, V, \Omega)\, du \ldots d\Omega.$$

As in the case of the spheres we may, without loss of generality, confine our attention to pairs whose line of centres is parallel to any fixed line, say the axis of x, then if p and P be the perpendiculars from the centres of inertia upon that line of centres, the velocity of approach of the points of contact of any pair, about to collide at the instant considered, will be

$$u - p\omega - (U - P\Omega).$$

And therefore the number of collisions in the short time dt after the instant considered will be proportional to

$$\{u - U - (p\omega - P\Omega)\}\, dt \times f_1(u, v, \omega) f_2(U, V, \Omega)\, du \ldots d\Omega.$$

After collision let the several velocity-components be

represented by the same symbols as before collision with dashes affixed, the coordinates remaining unchanged, so that the number of pairs of disks which pass from the state $u,\ u+du,\ \Omega,\ \Omega+d\Omega$ to the state $u',\ u'+du' \ldots \Omega',\ \Omega'+d\Omega'$ in the time dt will be proportional to

$$\{u-U-(p\omega-P\Omega)\}\, f_1(u,v,\omega)\, f_2(U,V,\Omega)\, du \ldots d\Omega\, .\, dt.$$

But the number of disks, with any given velocity-components at any instant, is assumed to be the same as the number with those velocity-components reversed. Whence it follows that the number of pairs of disks which pass from the state $u'\,u'+du' \ldots \Omega'\,\Omega'+d\Omega'$ to the state $u,\ u+du \ldots \Omega,\ \Omega+d\Omega$ in the time dt must be proportional to

$$\{U'-u'-(P\Omega'-p\omega')\}\, f_1(u',v',\omega')\, f_2(U',V',\Omega')\, du' \ldots d\Omega' dt.$$

Hence the condition for permanence, so far as collisions between pairs of these two sets, one at a time are concerned, will be satisfied by the condition that

$$(u-U-(p\omega-P\Omega))\, f_1(u,v,w)\, f_2(U,V,W)\, du \ldots d\Omega$$

is equal to

$$\{U'-u'-(P\Omega'-p\omega')\}\, f_1(u',v',\omega')\, .\, f_2(U',V',\Omega')\, du' \ldots d\Omega'.$$

Also the relative radial velocity of the points of collision before impact must be equal, and of opposite sign, to the same relative velocity after impact.

Therefore $u-U-p\omega+P\Omega = U'-u'-P\Omega'+p\omega'$,

i.e. $u'+u-(U'+U)-p(\omega'+\omega)+P(\Omega'+\Omega)=0.$

Also we may prove that the differential products

$$du \ldots d\Omega \quad \text{and} \quad du' \ldots d\Omega'$$

are numerically equal.

For if R be the measure of the impulse at the colliding points, we have the equations

$$u'-u=-\frac{R}{m},\quad U'-U=\frac{R}{M},\quad v'=v,\quad V'=V,$$

$$\omega'-\omega=\frac{pR}{mk^2},\quad \Omega'-\Omega=-\frac{PR}{MK^2};$$

whence by substitution in the equation

$$u'+u-(U'+U)-p(\omega'+\omega)+P(\Omega'+\Omega)=0,$$

we get

$$R=\frac{2(u-U-p\omega-P\Omega)}{\frac{1}{m}+\frac{1}{M}+\frac{p^2}{mk^2}+\frac{P^2}{MK^2}}=\frac{u-U-p\omega+P\Omega}{D},\text{ suppose;}$$

$$\therefore\ u'=u-\frac{1}{mD}\{u-U-p\omega+P\Omega\},$$

$$U'=U+\frac{1}{MD}\{u-U-p\omega+P\Omega\},$$

$$\omega'=\omega+\frac{p}{mk^2D}\{u-U-p\omega+P\Omega\},$$

$$\Omega'=\Omega-\frac{P}{MK^2D}\{u-U-p\omega+P\Omega\}.$$

And the functional determinant giving the ratio between the differential products, $du'\ldots d\Omega'$ and $du\ldots d\Omega$, becomes

$$\begin{vmatrix} 1-\frac{1}{mD}, & \frac{1}{mD}, & \frac{p}{mD}, & -\frac{P}{MD} \\ \frac{1}{MD}, & 1-\frac{1}{MD}, & -\frac{p}{MD}, & \frac{P}{MD} \\ +\frac{p}{mk^2D}, & -\frac{p}{mk^2D}, & 1-\frac{p^2}{mk^2D}, & \frac{pP}{mk^2D} \\ -\frac{P}{MK^2D}, & \frac{P}{MK^2D}, & \frac{pP}{MK^2D}, & 1-\frac{P^2}{MK^2D} \end{vmatrix}$$

that is

$$1 - \frac{1}{mD} - \frac{1}{MD} - \frac{p^2}{mk^2D} - \frac{P^2}{MK^2D}$$

or $1-2$ or -1.

So that the condition sought for is reduced to

$$f_1(u, v, \omega) f_2(U, V, \Omega) = f_1(u', v', \omega') f_2(U', V', \Omega'),$$

leading, as in the two previous cases, to the result

$$f_1(u, v, \omega) = A_1 e^{-h T_1},$$
$$f_2(U, V, \Omega) = A_2 e^{-h T_2},$$

T_1 being the kinetic energy of the disk of the one set and T_2 that of the disk of the second set, h a constant for both sets of disks, and A_1, A_2 special constants for each of the sets, determined in terms of h by the condition

$$A_1 \iiint e^{-h\frac{m}{2}(u^2+v^2+k^2\omega^2)} du\, dv\, d\omega = N_1,$$

$$A_2 \iiint e^{-h\frac{M}{2}(U^2+V^2+K^2\Omega^2)} . dU\, dV\, d\Omega = N_2;$$

where the integrations are in all cases between the limits $-\infty$ and $+\infty$, and N_1 and N_2 represent the number of disks in each of the sets.

With this law of distribution it follows that the state remains permanent so far as collisions between disks of the 1 and 2 sets alone are concerned.

Similarly it may be proved that the permanence of the distribution, with corresponding laws for each separate set of disks, would not be affected by collisions between pairs of disks, one pair at a time, both selected from any one set. Whence a law of distribution ensuring permanence of distribution and unaffected by any collisions whatever, with only two disks in each collision, is, that the number of

disks in any set with velocities between u, $u+du$, v, $v+dv$, ω, ω, $\omega+d\omega$ should be

$$Ae^{-\frac{mh}{2}(u^2+v^2+k^2\omega^2)}du\,dv\,d\omega,$$

where

$$A\iiint e^{-\frac{mh}{2}(u^2+v^2+k^2\omega^2)}du\,dv\,dw$$

is equal to the number of disks in that set.

7.] In Articles 1 and 2 we considered the cases in which the constituents of the medium consisted either of a very great number of smooth elastic spheres, equal to each other in every respect, or of sets of such spheres, the mass and volume of those of one set not being necessarily the same as those of any other set, but the number of spheres in each separate set being very great; and we proved that there would be a permanent state, unaffected by collisions, provided the number of such constituents whose velocity-components u, v, w were intermediate between u and $u+du$, v and $v+dv$, w and $w+dw$ at any instant were given by the expression

$$Ae^{-hT}du\,dv\,dw,$$

T being the Kinetic Energy of the constituent, h a constant for all the sets of constituents, and A a constant for each particular set determined by the equation

$$A\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{-hT}du\,dv\,dw=N,$$

N being the total number of constituents in that set.

In Art. 6 a slightly varied hypothesis as to the constituents led to a similar result, and it was proved that for a medium in which the constituents were sets of smooth perfectly elastic circular disks limited to motion in their own plane, with the centre of figure of each disk not coincident

with the centre of inertia, there would be permanence, provided the number of constituents of each set, the velocity-components of whose centre of inertia (u, v) lay between u, $u+du$; v, $v+dv$, while the angular velocity lay between ω and $\omega+d\omega$, were given by the expression

$$Ae^{-hT}\,du\,dv\,d\omega,$$

T being the Kinetic Energy of each disk, h a general constant common to all the sets, and A a special constant for each set determined by the equation

$$A\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{-hT}\,du\,dv\,d\omega=N,$$

where N is the number of disks of that particular set.

Before we proceed to the establishment of a general proposition, including the particular cases just mentioned, it will be necessary to prove the following theorem.

8.] Let there be any material system whose state is defined by the n generalised coordinates $q_1 \dots q_n$ and the corresponding components of momenta $p_1 \dots p_n$, and let the system move in a field of conservative forces from the state $p_1 \dots p_n$, $q_1 \dots q_n$ to the state $p'_1 \dots p'_n$, $q'_1 \dots q'_n$ in the time t, so that each of the $2n$ variables $p'_1 \dots q'_n$ is a determinate function of the $2n+1$ variables $p_1 \dots p_n$, $q_1 \dots q_n$ and t, then if t be constant, the functional determinant

$$\begin{vmatrix} \dfrac{dp'_1}{dp_1} \cdots \dfrac{dp'_1}{dq_n} \\ \vdots \quad\quad \vdots \\ \dfrac{dq'_n}{dq_1} \cdots \dfrac{dq'_n}{dq_n} \end{vmatrix}$$

is numerically equal to unity, or the multiple differentials $dp_1 \dots dq_n$ and $dp_1' \dots dq'_n$ are numerically equal to each other.

For if S be the Hamiltonian Principal function of $q_1 \dots q_n$ $q'_1 \dots q'_n$ and t, we have $2n$ equations

$$\left.\begin{aligned} p_1 &= -\frac{dS}{dq_1} \quad \dots \quad p_n = -\frac{dS}{dq_n} \\ p'_1 &= \frac{dS}{dq'_1} \quad \dots \quad p'_n = \frac{dS}{dq'_n} \end{aligned}\right\}, \quad \dots \quad \text{(A)}$$

the differential coefficients being partial.

Let us in any expression $\phi(p'_1 \dots q'_n)\, dp'_1 \dots dq'_n$ change the variables from $p'_1 \dots p'_n\, q'_1 \dots q'_n$ to $q_1 \dots q_n\, q'_1 \dots q'_n$, and we get

$$dp'_1 \dots dq'_n = \Delta \,.\, dq_1 \dots dq'_n$$

where $$\Delta = \begin{vmatrix} \frac{d^2S}{dq_1 dq'_1} \cdots \frac{d^2S}{dq_n dq'_1}, \\ \vdots \qquad\quad \vdots \\ \frac{d^2S}{dq_1 dq'_n} \cdots \frac{d^2S}{dq_n dq'_n}, \end{vmatrix}$$

by the use of the second set of equations (A) (above).

Similarly we get

$$dp_1 \dots dq_n = \Delta' \,.\, dq_1 \dots dq'_n$$

where $$\Delta' = \begin{vmatrix} -\frac{d^2S}{dq'_1 dq_1} \cdots -\frac{d^2S}{dq'_n dq_1} \\ \vdots \qquad\quad \vdots \\ -\frac{d^2S}{dq'_1 dq_n} \cdots -\frac{d^2S}{dq'_n dq_n} \end{vmatrix} = (-1)^n \,.\, \Delta,$$

by the use of the first set of equation (A)*.

Whence we get $dp_1 \dots dq_n$ numerically equal to $dp'_1 \dots dq'_n$.

* The original Edition of this book contained a supposed demonstration of a proposition analogous to that in the text but the reasoning was fallacious.

In the proposition referred to the initial and final coordinates and momenta were supposed to be connected by the condition E (the total energy) constant and not t (the interval of time between the two states)

9.] Let there be any number of sets of perfectly smooth elastic rigid bodies of any form, henceforth called molecules,

constant, and the demonstration was in all respects the same as that in the text, with the substitution of the Hamiltonian Characteristic function A for the Principal function S, so that the result took the form

$$\frac{dp'_1 \dots dq'_n}{dp_1 \dots dq_n} = \frac{(\Delta)}{(\Delta')},$$

where (Δ) and (Δ') were the Δ and Δ' in the text with A substituted for S, and therefore numerically equal to each other; and so far the demonstration was correct, but in fact, in this case, Δ and Δ' are each separately zero.

For the momenta components $p_1 \dots p_n$, with which the system must be started, in order to pass from the initial position $q_1 \dots q_n$ to the final position $q'_1 \dots q'_n$ with a given energy E must be the same for all values of $q'_1 \dots q'_n$, provided they be consistent with any configuration whatever through which the system passes either before or after reaching the actual final configuration, or

$$\frac{dp_1}{dq'_1}\dot{q}'_1 + \frac{dp_1}{dq'_2}\dot{q}'_2 + \&c. + \frac{dp_1}{dq'_n}\dot{q}'_n = 0,$$

where $\dot{q}'_1$, $\dot{q}'_2$, &c. are the time variations of q'_1, q'_2, &c. in the actual motions, with similar equations when p_2, p_3, &c. are substituted for p_1.

Whence we have

$$\begin{vmatrix} \frac{dp_1}{dq'_1} & \dots & \frac{dp_1}{dq'_n} \\ \vdots & & \vdots \\ \frac{dp_n}{dq'_1} & \dots & \frac{dp_n}{dq'_n} \end{vmatrix} = 0,$$

or $(\Delta') = 0$, and similarly $(\Delta) = 0$.

Whence it follows that if the initial and final states be connected by the condition E constant, we can get no determinate relation between the differential products $dp'_1 \dots dq'_n$ and $dp_1 \dots dq_n$, and this conclusion might have been anticipated, because from the equations of motion we get $2n$ equations among the $2n+1$ variables $p'_1 \dots p'_n\ q'_1 \dots q'_n$, $p_1 \dots p_n$, $q_1 \dots q_n$ and t (the time of transit), and we need an additional relation between them to determine each of the $2n$ variables $(p'_1 \dots q'_n)$ in terms of

$$(p_1 \dots p_n\ q_1 \dots q_n).$$

But the condition E constant does not supply any such additional relation, so that the problem remains indeterminate. The fallacy just noticed in the original edition was first of all pointed out by Boltzmann in a communication to the Philosophical Magazine in 1882, when I privately suggested to him the substitution of the proposition in the text. In a communication to the same magazine in 1891, Lord Rayleigh independently advanced a similar objection to that of Boltzmann against the original treatment and proposed the same amendment.

in motion in a region inclosed within a perfectly elastic boundary, let, also, the molecules in each set be exactly similar to each other in all respects, while those of different sets may differ in any respect, viz. as to shape, volume, mass, &c., subject, at least, to the condition that the volume of each molecule is infinitely small compared with that of the inclosed region, and that the number of molecules in each set is very large, then the state of the medium so constituted will be permanent and unaffected by collisions between two molecules, either of the same or different sets, provided the law of distribution be such that the number of molecules of any set whose momenta and coordinates are intermediate between p_1 and $p_1+dp_1 \ldots q_m$ and q_m+dq_m be of the form

$$Ae^{-hT}\,dp_1 \ldots dq_m,$$

where m is the number of degrees of freedom of the molecule and therefore lying between 3 and 6 inclusive, T is the kinetic energy of the molecule, h a constant the same for all sets, and A a special constant for each set determined by the condition that

$$A\iint \ldots e^{-hV}\,dp_1 \ldots dq_m$$

shall be equal to the number of molecules in the set considered, the integrations having taken over all possible values of the variables.

In the first place it is evident that this law of distribution will be permanent, in the absence of collisions, because in such a case T remains constant for all time for each molecule, and so also does the multiple differential

$$dp_1 \ldots dq_m$$

by the last Article.

Neither will the distribution be affected by collisions between any pair of molecules either of the same or

different sets. For, according to this law, the number of molecules of any one set with coordinates intermediate between q_1 and $q_1+dq_1 \dots q_m$ and q_m+dq_m, and momenta between p_1 and $p_1+dp_1 \dots p_m$ and p_m+dp_m, is

$$Ae^{-hT}\,dq_1 \dots dq_m\,dp_1 \dots dp_m.$$

Let us suppose m to have its greatest possible value 6, and let q_1, q_2, q_3 be the rectangular coordinates x, y, z of the centre of inertia, and q_4, q_5, q_6 be the ordinary Eulerian angular coordinates θ, ϕ, ψ, determining the orientation of the molecule about the centre of inertia, then if u, v, w be the translational velocity-components of the centre of inertia and ω_1, ω_2, ω_3 the angular velocities about the principal axes through that point and M the mass of each molecule, p_1, p_2, p_3 are equal to Mu, Mv, Mw, respectively, and p_4, p_5, p_6 are each linear functions of ω_1, ω_2, ω_3, so that by elimination of $p_1 \dots p_6$ the number of molecules of this set with coordinates between x, $x+dx \dots \psi$, $\psi+d\psi$, and translational and angular velocities between u, $u+du \dots \omega_3$, $\omega_3+d\omega_3$, is by the assumed law

$$Ae^{-hT}\chi(\theta, \phi, \psi)\,dx \dots d\psi\,du \dots d\omega_3,$$

where $$T=\frac{M}{2}\{u^2+v^2+w^2+k_1^2\,\omega_1^2+k_2\,\omega_2^2+k_3^2\,\omega_3^2\},$$

k_1, k_2, k_3 being radii of gyration about the principal centre of inertia axes.

Integrating for all values of $x \dots \psi$ we get

$$A_1\,e^{-hT}\,du \dots d\omega_3$$

for the number of molecules of the set in question with velocities intermediate between u, $u+du$, …, ω_3, $\omega_3+d\omega_3$, T having the same value as before, and A_1 being determined by the condition

$$A_1\iiint \dots e^{-hT}\,du \dots d\omega_3 = N,$$

where N is the number of molecules in the set in question.

This expression is perfectly general and applies to all forms of the molecules and all numbers of degrees of freedom ; for example, when they are smooth spheres the k's are all equal and $\omega_1^2 + \omega_2^2 + \omega_3^2$ for each sphere is constant, so that the law reduces to the statement that

$$Ae^{-hT}\,du\,dv\,dw$$

is the number with translational velocities between $u, u+du$, $v, v+dv$, $w, w+dw$, the number of degrees of freedom being 3 as in Arts. 1 and 3.

When the molecules are straight bars, one of the k's becomes zero, and the corresponding ω does not affect the state of the molecule, and the number of degrees of freedom is 5, and so on.

By our assumed law of distribution for all the sets, the number of pairs of molecules of any two sets, say the A and B sets, which at any instant have their velocities between the limits $u, u+du, \ldots \omega_3, \omega_3+d\omega_3$ for the one, and $U, U+dU, \ldots \Omega_3$ and $\Omega_3+d\Omega_3$ for the other, is

$$ABe^{-h(T_A+T_B)}\,du \ldots d\Omega_3,$$

and the rate of collision, per unit time, of these two molecules is ν, where r is the relative velocity of approach of the colliding points, in the direction of the common normal at these points, at the instant of collision, so that the number of this particular class of collisions, between the pairs, in the time dt, will be

$$ABe^{-h(T_A+T_B)}\,du \ldots d\Omega_3\,\nu\,dt.$$

After collision let the velocities be denoted by affixing dashes to the symbols which denote the respective velocities before collision, whence it follows that the number of pairs of molecules, given by the last written expression, passes

from the state u, $u+du \ldots \Omega_3$, $\Omega_3+d\Omega_3$ to the state

$$u', u'+du' \ldots \Omega'_3, \Omega'_3+d\Omega'_3$$

in time dt, by this particular kind of collision.

It follows by reasoning in all respects similar to that employed in the cases already treated that the number of molecule pairs passing from the state

$$u', u'+du', \ldots \Omega'_3, \Omega'_3+d\Omega'_3$$

to the state u, $u+du \ldots \Omega_3$, $\Omega_3+d\Omega_3$ in the same time dt is

$$ABe^{-h(T'_A+T'_B)}\, du' \ldots d\Omega'_3\, v' dt,$$

where v' is the same function of $-u' \ldots -\Omega'_3$ that v is of $u \ldots \Omega_3$ since the coordinates are unchanged by collision, i. e. where v' is the reversed relative velocity of the colliding points in the direction of the common normal.

But since the elasticity is perfect we have

$$v' = v,$$

also

$$T'_A + T'_B = T_A + T_B.$$

Therefore the condition sufficient for permanence, so far as this particular kind of collision between the molecule pair is concerned, is reduced to

$$du \ldots d\Omega_3 = du' \ldots d\Omega'_3.$$

But by D'Alembert's principle applied to impulsive forces we have the equations

$$\frac{u'-u}{\lambda_1} = \frac{v'-v}{\lambda_2} \ldots = \frac{\Omega'_3-\Omega_3}{\lambda_{12}} = R,$$

where $\lambda_1 \ldots \lambda_{12}$ are known functions of the q's and Q's.*

* It is easily seen that the condition of collision is

$$\xi(q_1 \ldots q_n) = 0,$$

where $q_1 \ldots q_n$ are all the coordinates of the two colliding molecules and ξ is a function of these coordinates which cannot become negative, whence it will follow that λ_1, λ_2, &c. are proportional to $\frac{d\xi}{dq_1}$, $\frac{d\xi}{dq_2}$, &c.

Now v is a linear function of $u \ldots \Omega_3$ of the form

$$v = \mu_1 u \ldots + \mu_6 \Omega_3,$$

and v' is the same function of $-u' \ldots, -\Omega'_3$ and is equal to v, whence to determine R we have the equation

$$\mu_1 (u' + u) + \mu_2 (v' + v) \ldots + \mu_{12} (\Omega'_3 + \Omega_3) = 0,$$

i.e. $2 (\mu_1 u + \mu_2 v \ldots + \mu_{12} \Omega_3) + R (\lambda_1 \mu_1 + \lambda_2 \mu_2 \ldots + \lambda_{12} \mu_{12}) = 0.$

Whence we get the 6 equations

$$u' = u - \frac{2\lambda_1 (\mu_1 u \ldots + \mu_{12} \Omega_3)}{\lambda_1 \mu_1 \ldots + \lambda_{12} \mu_{12}},$$

$$\vdots \qquad\qquad \vdots$$

$$\Omega'_3 = \Omega_3 - \frac{2\lambda_{12} (\mu_1 u \ldots + \mu_{12} \Omega_3)}{\lambda_1 \mu_1 \ldots + \lambda_{12} \mu_{12}}.$$

Therefore (writing $2D$ for $\lambda_1 \mu_1 + \ldots + \lambda_{12} \mu_{12}$) the ratio of $du' \ldots d\Omega'$ to $du \ldots d\Omega_3$ is equal to the determinant

$$\begin{vmatrix} 1 - \frac{\lambda_1 \mu_1}{D}, & -\frac{\lambda_1 \mu_2}{D} \ldots & -\frac{\lambda_1 \mu_{12}}{D} \\ -\frac{\lambda_2 \mu_1}{D}, & 1 - \frac{\lambda_2 \mu_2}{D} \ldots & -\frac{\lambda_2 \mu_{12}}{D} \\ \cdots & \cdots & \cdots \\ -\frac{\lambda_{12} \mu_1}{D}, & -\frac{\lambda_2 \mu_2}{D} \ldots & 1 - \frac{\lambda_1 \mu_{12}}{D} \end{vmatrix}$$

$$= 1 - \frac{\lambda_1 \mu_1}{D} - \frac{\lambda_2 \mu_2}{D} \ldots - \frac{\lambda_1 \mu_{12}}{D}$$

$$= -1.$$

Or the multiple differentials $du \ldots d\Omega_3$ and $du' \ldots d\Omega'_3$ are numerically equal to each other, and the assumed law of distribution, if once established, is unaffected by collisions between any pair of molecules whatever; we have seen

also that it is maintained in the absence of collisions, and it is therefore permanent.

The number of what is here called *kinds of collision* between any molecule pair is infinitely great; in the case of spheres these kinds of collisions differ from each other only in the direction of the common normal to the surfaces at the colliding points, in a sphere and an ellipsoid they will differ, not only in this circumstance, but also in the orientation of the ellipsoid at the instant of collision, and in the case of two ellipsoids they may differ in the orientation of both ellipsoids, but this variety in the kinds of collision does not affect the reasoning in the text.

10.] In the last Article the problem of collision between two molecules has been treated by the assumptions ordinarily employed in rigid dynamical problems of collision between two perfectly elastic solids of any form, and all that is necessary to the validity of the result arrived at, is the fact of the independence of the quantities λ_1, λ_2, &c. of the momenta at the instant of collision, without reference to the actual value of these λ's. By a slight change however in the language and conceptions employed, the λ's may be evaluated and the results arrived at may be extended from rigid molecules with a maximum of 6 degrees of freedom each, to molecules of any form and any number of degrees of freedom, as for example a chain of r links, in which the number of degrees of freedom is $2r+3$, and other systems.

For, by Lagrange's equations, if T be the kinetic energy of any system expressed as a quadratic function of the $\dot{q}$'s with coefficients functions of the q's, and U be the force function, we have

$$\frac{d}{dt}\cdot\frac{dT}{d\dot{q}} - \frac{dT}{dq} = \frac{dU}{dq}.$$

If in such a system there be finite change of velocities, or momenta in a very short time t, without finite change of coordinates, in other words a collision, we get by integration

$$\left(\frac{dT}{d\dot{q}}\right)^{t_2} - \left(\frac{dT}{d\dot{q}}\right)^{t_1} = \int_{t_1}^{t_2} \frac{dU}{dq},$$

where $t_2 - t_1 = t$, since $\int_{t_1}^{t_2} \left(\frac{dT}{dq}\right) =$ zero in the limit when $t_2 - t_1$ is infinitely small, because in the general case $\frac{dT}{dq}$ must throughout the integration be intermediate between two finite quantities (see Routh's *Rigid Dynamics* (Art. 372, Third Edition, Watson and Burbury's *Generalised Coordinates* (Art. 12), &c.).

That is to say,

$$p'_1 - p_1 = \int_{t_1}^{t_2} \frac{dU}{dq_1} \dots p'_n - p_n = \int_{t_1}^{t_2} \frac{dU}{dq_n}.$$

Now collisions, or finite changes of momenta with unchanged coordinates, can only be regarded as occurring when the system arrives at a configuration determined by such a condition as

$$\phi(q_1 \dots q_n) = 0,$$

where ϕ is a function of the q's which cannot change sign, or in other words, the system and forces are such that there is an infinitely great force resisting such change of sign.

Now U, the assumed force function of the forces, is a determinate function of the n coordinates $q_1, \dots q_n$, and therefore may be expressed as a determinate function of ϕ and $n-1$ quantities chosen arbitrarily as $\phi_1, \phi_2 \dots \phi_{n-1}$, and from the last paragraph it follows that if U be so expressed $\frac{dU}{d\phi}$ must be infinitely great when $\phi = 0$, and

therefore, when $\phi = 0$, $\frac{dU}{dq_1}, \frac{dU}{dq_2}$ &c. must be proportional to

$$\frac{d\phi}{dq_1}, \frac{d\phi}{dq_2}, \text{ &c.,}$$

and therefore we get n equations of the general form

$$p' - p = \int_{t_1}^{t_2} \frac{dU}{d\phi} \cdot \frac{d\phi}{dq} = \frac{d\phi}{dq} \cdot \int_{t_1}^{t_2} \frac{dU}{d\phi},$$

since ϕ is a function of the q's only and independent of the $\dot{q}$'s. Whence it follows that λ_1, λ_2 are proportional to $\frac{d\phi}{dq_1}, \frac{d\phi}{dq_2}$, &c., *and therefore independent of the p's.*

By supposing a system made up of two molecules of this more general constitution, with m and n degrees of freedom, respectively, in the place of the 6 degrees of freedom each of the last Article, we get, as in that Article, the $m+n-1$ equations

$$\frac{p'_1 - p_1}{\frac{d\phi}{dq_1}} = \frac{p'_2 - p_2}{\frac{d\phi}{dq_2}} \text{ &c.} = \frac{p'_{m+n} - p_{m+n}}{\frac{d\phi}{dq_{m+n}}},$$

the λ_1, λ_2, &c. being replaced by $\frac{d\phi}{dq_1}, \frac{d\phi}{dq_2}$, &c.

Also since by our hypothesis there is no change of Kinetic Energy, we have the additional equation

$$\Sigma \frac{dU}{dq} \frac{(\dot{q}' + \dot{q})}{2} = 0,$$

or since by the reasoning above given $\frac{dU}{dq}$ is sensibly equivalent to $\frac{dU}{d\phi} \cdot \frac{d\phi}{dq}$, we get

$$\Sigma \frac{d\phi}{dq} \cdot (\dot{q}' + \dot{q}) = 0.$$

Now $\Sigma \frac{d\phi}{dq}\dot{q} = \left(\frac{d\phi}{dt}\right)$ and $\Sigma \frac{d\phi}{dq}\dot{q}' = \left(\frac{d\phi}{dt}\right)'$.

So that we get the equation

$$\dot{\phi} + \dot{\phi}' = 0,$$

the equivalent to $\nu + \nu' = 0$ of the last Article.

Whence it follows, by reasoning in all respects the same as that of the last Article, with the substitution of m and n for 6 and 6 respectively, that the functional determinant expressing the ratio of the multiple differentials

$$dp_1 \dots dp_{m+n} \text{ and } dp'_1 \dots dp'_{m+n}$$

is numerically equal to unity, and since $\dot{\phi}$ measures the rapidity of entry into the colliding state it will further follow that a law of distribution for each set of molecules thus generalised of the form

$$Ae^{-hT} dp_1 \dots dq_m$$

for the number of that set with momenta and coordinates between p_1 and $p_1 + dp_1 \dots q_m$ and $q_m + dq_m$ will be permanent in the absence of collisions, or in spite of collisions between molecules (two at a time), either of the same or different sets.

The expression of the law may also be conveniently modified as in the last Article, for since T is an essentially positive quadratic function of the p's with coefficients functions of the q's, it may, by suitable linear transformations of the p's, be expressed in the form

$$r^2_1 \dots + r^2_m,$$

so that the law of distribution assumes the form

$$f(q_1 \dots q_m)\, e^{-h(r_1^2 + \&c. + r^2_m)}\, dr_1 \dots dr_m\, dq_1 \dots dq_m.$$

And then integrating for all values of the q's, the law in question becomes that the number of molecules of this set for which the r's lie between r_1 and $r_1 + dr_1 \ldots r_m$, and $r_m + dr_m$

$$\text{is } Ae^{-h\Sigma(r^2)}.\, dr_1 \ldots dr_m,$$

where h is constant for all sets and

$$A\iiint \ldots e^{-h\Sigma(r^2)}\, dr_1 \ldots dr_m$$

is equal to the total number of molecules of this particular set.*

11.] Let there be any number of sets of perfectly smooth and perfectly elastic molecules, of any form and any number of degrees of freedom, in motion in a region inclosed within a perfectly elastic boundary, as in the last Article, let also the inclosed region be a field of forces towards fixed centres acting on the molecules, then the state of the medium will be permanent in the absence of collisions, and will be unaffected by collisions between any two molecules, whether of the same or different sets, provided the law of distribution be such that the number of molecules in any set with momenta components intermediate between p_1 and $p_1 + dp_1 \ldots p_m$ and $p_m + dp_m$, and coordinates intermediate between q_1 and $q_1 + dq_1 \ldots q_m$ and $q_m + dq_m$ be

$$Ae^{-hE}\, dp_1 \ldots dq_m,$$

* In the treatment in the text the impulsive collision forces have been regarded as ordinary force function forces which become infinite in the colliding configuration. We may also regard the collision under the aspect of an impact whose generalised components are I_1, I_2, &c., where I_1, I_2, &c. are subject to the condition

$$I_1 dq_1 + I_2 dq_2 \ldots + I_n dq_n = 0$$

whenever

$$\frac{d\phi}{dq_1} dq_1 + \frac{d\phi}{dq_2} dq_2 + \frac{d\phi}{dq_n} dq_n = 0,$$

leading to the same result, or

$$I_1 : I_2 \text{ &c., } :: \frac{d\phi}{dq_1} : \frac{d\phi}{dq_2} \text{ &c.}$$

m being the number of degrees of freedom of the molecule, E its *total* energy potential and kinetic, h a constant the same for all sets of molecules, and A a constant for each particular set determined by the condition that

$$A \iiint \dots e^{-E} dp_1 \dots dq_m$$

is equal to the number of the molecules in the set considered, the integrations being taken over all possible values of the p's and q's.

For, in the first place, it is clear that the law is permanent in the absence of collisions, inasmuch as the values of E and the multiple differential $dp_1 \dots dq_m$ are separately constant in this case by the law of conservation of mechanical energy, and by Art. 8.

In the next place, such permanence will be unaffected by collisions between any two of the molecules, for the reasoning of the last Article is in no respect affected by the substitution of E for T; whence the proposition is proved.

In the previous Articles the position of a molecule did not enter into consideration but only the values of the momenta components, so that the condition of the molecule was fully determined by the limits p_1, $p_1 + dp_1$, &c. of these components, and these limits for each molecule are clearly independent of those of all the rest.

It is otherwise however with the coordinates of position of the centre of inertia of a molecule, for if the molecular volumes be appreciable, these coordinates for any molecule will not be independent of those of the rest, unless the sum of the molecular volumes in a unit of volume be a very small fraction. Since however the disregard of all but binary collisions involves the same condition the reasoning remains the same as before.

Again, the condition of interchange of the molecules

after collision cannot of course be *exactly* satisfied in this case, and the reasoning would fail unless the size of the molecules were so small that the potential was sensibly unaltered for a distance comparable with the linear dimensions of each molecule, or, at least, unless the variation of the quantity $h\chi$ was inappreciable for such distances.

In all the cases, however, contemplated in this treatise the Kinetic Energy largely preponderates over the potential, or $h\delta\chi$ will be absolutely insensible for such variation of χ in comparison with $h(\chi + T)$.

In dealing with the so-called rigid elastic molecule with 6 degrees of freedom as a maximum we regard it under the ordinary conventional aspect of a body whose parts are incapable of relative displacement, so that there is no gain or loss of potential energy of mutual forces between these parts, or, as they may be called, interatomic forces; but in passing to the more general conception of a molecule such interatomic forces, with the corresponding variation of interatomic potential, must be taken into account.* Their presence will not affect the reasoning in the text because for any single molecule Ae^{-hE} will be constant in the intervals between collisions where E is the *total* Energy of the molecule, and the differential product

$$dp_1 \dots dq_m$$

will also be constant by Art. 8, while during collision *all* the coordinates, and therefore also the interatomic potential energy, are unchanged. It is to be remembered also that no account is taken of other than binary collisions, in other words, it is assumed that the chance of three or more molecules being in collision simultaneously is infinitely less than

* For instance, our molecules might be conceived as made up of discrete material particles acted on by mutual forces, or as bodies with a certain limited number of degrees of freedom between the parts of which there are still mutual forces but with a limited number of generalised components of force.

that of binary encounters, necessitating the postulate tacitly made in all cases that the sum total of the volume of the molecules in any region is very much less than the volume of that region.

12.] Hitherto we have viewed the collisions between our elastic molecules under the ordinary conventional aspect, in which there is an infinitely large force acting for a time absolutely insensible, and therefore accompanied by no change of the coordinates. The truer view, as already pointed out, would be to consider the force called into play by a collision as very large but not absolutely infinite, and the time of such collision as very small although not absolutely evanescent, and such that changes of value of the coordinates during collision are not absolutely excluded. The collision viewed under such an aspect we call an *encounter*; if the number and size of the molecules be sufficiently restricted it may still be true that the chance of a binary encounter is infinitely larger than that of a multiple encounter, and under such conditions all but binary encounters may be neglected. We proceed now to show that the $e^{-h(\alpha+T)}$ law holds for encounters as well as for collisions.

If a material system in a field of conservative forces having the n generalised coordinates $q_1 \dots q_n$ and the corresponding momentum components $p_1 \dots p_n$ move from the state $q_1, q_1+dq_1 \dots p_n, p_n+dp_n$ to the state

$$q'_1, q'_1+dq'_1 \dots p'_n, p'_n+dp'_n,$$

where the states are connected by the relation $q_n - q'_n = C$ (any constant), then the functional determinant.

$$\begin{vmatrix} \frac{dp'_1}{dp_1} & \dots & \frac{dp'_1}{dq_{n-1}} \\ \vdots & & \vdots \\ \frac{dp'_{n-1}}{dp_1} & \dots & \frac{dq'_{n-1}}{dq_{n-1}} \end{vmatrix}$$

is numerically equal to $\frac{\dot{q}_n}{\dot{q}'_n}$, where the dot indicates time variation, or which is the same thing,

$$dp'_1 \dots dq'_{n-1} = \frac{\dot{q}_n}{\dot{q}'_n} dp_1 \dots dq_{n-1} \text{ numerically.}$$

For we know by Art. 8 that if the two states dashed and undashed be connected by the relation t is constant, where t is the interval of time taken to pass from one to the other,

$$dp_1 \dots dq_n = dp'_1 \dots dq'_n \text{ numerically.}$$

From the equations of motion we can obtain two equations of the form

$$q_n = f(p'_1 \dots q'_n,\ t), \quad q'_n = F(p_1 \dots q_n,\ t),$$

where f and F are determinate functions.

Interchange the variables q_n and t in the multiple differential

$$dp_1 \dots dq_n$$

and it becomes

$$dp_1 \dots dq_{n-1} \frac{df}{dt} . dt,$$

where $p'_1 \dots q'_n$ are constant in obtaining $\frac{df}{dt}$.

But $\frac{df}{dt}$ so obtained is equal to $\dot{q}_n$.

And therefore

$$dp_1 \dots dq_n = dp_1 \dots dq_{n-1}\, \dot{q}_n\, dt.$$

Similarly, expressing q'_n in terms of t, we get

$$dp'_1 \dots dq'_n = dp'_1 \dots dq'_{n-1} \frac{dF}{dt},$$

where $p_1 \dots q_n$ are constant in obtaining $\frac{dF}{dt}$, and therefore

$$\frac{dF}{dt} = -\dot{q}'_n;$$

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therefore $dp'_1 \dots dq'_n = dp'_1 \dots dq'_{n-1}\, \dot{q}'_n\, dt$ numerically,

therefore

$$dp_1 \dots dq_{n-1}\, \dot{q}_n\, dt = dp'_1 \dots dq'_{n-1}\, \dot{q}'_n\, dt \text{ numerically},$$

because the time from $p_1 \dots q_n$ to $p'_1 \dots q'_n$ is the same as that from $p'_1 \dots q'_n$ to $p_1 \dots q_n$ with reversed velocities.

Therefore

$$dp_1 \dots dq_{n-1}\, \dot{q}_n = dp'_1 \dots dq'_{n-1}\, \dot{q}'_n \text{ numerically},$$

or

$$\frac{dp_1 \dots dq_{n-1}}{dp'_1 \dots dq'_{n-1}} = \frac{\dot{q}'_n}{\dot{q}_n} \text{ numerically.}*$$

* This proposition has been proved by Boltzmann by the evaluation of the functional determinant

$$\begin{vmatrix} \frac{dp'_1}{dp_1} & \dots & \frac{dp'_1}{dq_n} \\ \vdots & & \vdots \\ \frac{dq'_n}{dp_1} & \dots & \frac{dq'_n}{dq_n} \end{vmatrix},$$

and in a similar way by Burbury.

An interesting illustration is afforded by a trajectory traversing a closed curve or surface.

If one of the two coordinates q_1, q_2 in the case of a plane trajectory, as q_2, be the distance of the point from the curve, then it will follow that

$$\frac{dp_1\, dp_2\, dq_1}{dp'_1\, dp'_2\, dq'_1} = -\frac{\dot{q}_2}{\dot{q}'_2}.$$

For example, if the curve be a circle and the trajectory be referred to polar coordinates r, θ, the centre of the circle being the pole,

$$p_1 = r\frac{d\theta}{dt}, \quad p_2 = \frac{dr}{dt}, \quad q_1 = \theta, \quad q_2 = r.$$

Then the proposition states that when $r = r'$, the determinant

$$\begin{vmatrix} \frac{dp'_1}{dp_1} & \frac{dp'_1}{dp_2} & \frac{dp'_1}{dq_1} \\ \frac{dp'_2}{dp_1} & \frac{dp'_2}{dp_2} & \frac{dp'_2}{dq_1} \\ \frac{dq'_1}{dp_1} & \frac{dq'_1}{dp_2} & \frac{dq'_1}{dq_1} \end{vmatrix} = \frac{\dot{q}_2}{\dot{q}'_2} \text{ numerically.}$$

A result which may be easily verified for a projectile.

In obtaining the ratio of the multiple differentials we suppose $p'_1 \dots q'_n$ to be found in terms of $p_1 \dots q_n$ and t from the $2n$ equations of motion

$$p'_1 = f_1(p_1 \dots q_n, t) \dots q'_n = f_{2n}(p_1 \dots q_n, t),$$

and then introduce the equation $q'_n = q_n + C$, regarding both q_n and C as constants, thereby lowering the number of independent variables from $2n$ to $2n-1$, and really evaluating the functional determinant

$$\begin{vmatrix} \frac{dp'_1}{dp_1} & \cdots & \frac{dp'_1}{dq_{n-1}} \\ \vdots & & \vdots \\ \frac{dq'_{n-1}}{dp_1} & \cdots & \frac{dq'_{n-1}}{dq_{n-1}} \end{vmatrix}.$$

13.] So far we have proved that when sets of molecules are in motion in a region, the molecules in each set having any number of degrees of freedom, and all being acted on by forces, fixed-central or interatomic, then the law of distribution

$$Ae^{-hE}\, dp_1 \dots dq_m,$$

for any set of molecules, will be unaffected by collisions regarded as of no sensible duration.

We may now prove that this permanence will be unaffected by *encounters* between molecules, two at a time, whether of the same or of different sets.

For if the coordinates of one of two molecules with m degrees of freedom be denoted by $q_1 \dots q_m$, and those of the other with n degrees of freedom be denoted by

$$q_{m+1} \cdots q_{m+n},$$

then the condition of an encounter between the two mole-

cules may be regarded as defined by an equation among the coordinates of the form

$$\phi(q_1 \dots q_{m+n}) = 0.$$

Let ϕ be taken for one of the coordinates, say q_{m+n} of the two molecules, then by reasoning exactly as in the previous propositions, it will follow that if, in any encounter between such a pair of molecules, p, q pass to p', q', the number of pairs of molecules passing from the limits p and $p+dp$, q and $q+dq$ to p' and $p'+dp'$, q' and $q'+dq'$ will be

$$e^{-h(E+E')}\, dp_1 \dots dq_{m+n-1}\, \dot{q}_{m+n}\, dt$$

in any short time dt, and also that the number passing from the limits $-p'$ and $-(p'+dp')$, q' and $(q'+dq')$ to p and $p+dp$, q and $q+dq$ in the same time, will be

$$e^{-h(E+E')}\, dp'_1 \dots dq'_{m+n-1}\, \dot{q}'_{m+n}\, dt.$$

And these numbers are equal by the last Article, whence the proposition is proved.

Hence we conclude from this and the previous Articles that with the most general conceivable construction of our sets of molecules, subject at least to restrictions already noticed as to number and size, the law of distribution,

$$Ae^{-hE}\, dp_1 \dots dq_m,$$

for each set of molecules, will, when once attained, be a permanent law.

The total energy E is of the form $\chi + T$, where χ is the potential energy of the molecule in the force field, inclusive of interatomic forces, at any instant, with the values which the coordinates of that molecule have at that instant, and is therefore a known function of the q's of that molecule, T is the kinetic energy of the molecule, and therefore is expressible in the form

$$\frac{M}{2}\{u^2 + v^2 + w^2 + r_4^2 + \dots + r_m^2\},$$

M being the mass, u, v, w the component velocities of the centre of inertia of the molecule, and $r_4 \dots r_m$ linear functions of the p's with coefficients functions of the q's. Hence by simple transformations the number of molecules of the set under consideration, with variables lying between the limits

$$q_1, q_1 + dq_1 \dots r_m, r_m + dr_m,$$

may be written in the form

$$\psi(q_1 \dots q_m)\, e^{-h\left(\chi + \frac{M}{2}(u^2 + \dots + r_m^2)\right)}\, dq_1 \dots dq_m\, du \dots dr_m,$$

and integrating for all values of the q's, the total number of molecules, of the set in question, with the $u \dots r_m$ variables lying between the limits u, and $u + du, \dots, r_m$, and $r_m + dr_m$ becomes

$$A e^{-\frac{Mh}{2}(u^2 + \dots + r_m^2)}\, du \dots dr_m,$$

where h is a constant, the same for all the sets of molecules, and A is a constant, differing for different sets and satisfying, for each set of N molecules, the equation

$$A \iint \dots e^{-\frac{Mh}{2}(u^2 + \dots + r_m^2)}\, du \dots dr_m = N.$$

From this it follows that the average value of each of the magnitudes $\frac{Mu^2}{2}$, $\frac{Mv^2}{2}$, ..., $\frac{Mr_m^2}{2}$ is $\frac{1}{2h}$, and that the average value of the total kinetic energy of each molecule is $\frac{m}{2h}$.

14.] In the preceding Articles we have proved that the e^{-hE} law of distribution is, subject to certain stated limitations, *sufficient* for the permanence of distribution, we now proceed to prove, by means of a proposition due to Boltzmann, that this law is not only sufficient but also necessary.

Let there be any number of sets of molecules circumstanced as in the preceding Articles, and let the distribution of the coordinates and momenta of any one of the sets, with m degrees of freedom, be such that the number of the molecules of that set, with momenta and coordinates intermediate between P_1 and $P_1+dP_1 \dots Q_m$ and Q_m+dQ_m, is

$$F(P_1 \dots Q_m)\, dP_1 \dots dQ_m.$$

Also let the corresponding distribution for any other set with (n) degrees of freedom be expressed by

$$f(p_1 \dots q_n)\, dp_1 \dots dq_n,$$

F and f being any determinate functions. Let also any P' and Q', p' and q' be connected with the corresponding P and Q, p and q by the relation that P, Q, p, q are changed into P', Q', p', q' respectively by an encounter between the two molecules, and for brevity let $F(P_1 \dots Q_m)$ and $F(P'_1 \dots Q'_m)$ be denoted by F, F', with corresponding meanings for f and f'. Then there exists a function H such that the time variation $\dfrac{dH}{dt}$ is always negative, unless the condition

$$Ff = F'f'$$

be satisfied for every combination, two and two, of the sets of molecules, including pairs of molecules both of the same set, that is, including the case

$$F(P_1 \dots Q_m)\, F(p_1 \dots q_m) = F(P'_1 \dots Q'_m)\, F(p'_1 \dots q'_m).$$

In the first place, let us regard the medium as consisting of only two sets of molecules with m and n degrees of freedom respectively, and with the distribution laws F and f, then the number of encounters per unit of time between pairs of molecules, one from each set, with momenta and coordinates between P and $P+dP$, Q and $Q+dQ$, p and $p+dp$, q and $q+dq$ will be

$$F.f.\, dP_1 \dots dq_{n-1}\, \dot{q}_n,$$

provided the coordinate q_n be chosen so that $q_n = 0$ is a condition of the beginning or end of an encounter, and q_n be made equal to 0 wherever it occurs in $f(p_1 \dots q_n)$.

And therefore the expression

$$F.f\,dP_1 \dots dq_{n-1}\,\dot{q}_n$$

is the number of pairs of molecules, one from each of these sets passing from the state $P,\ P+dP \dots q,\ q+dq$ to the state $P',\ P'+dP' \dots q',\ q'+dq'$ per unit of time, when q_n is put equal to 0 in f.

Similarly the number of pairs passing from the state $P',\ P'+dP' \dots q',\ q'+dq'$ to the state $P,\ P+dP \dots q,\ q+dq$ per unit of time, will be

$$F'.f'\,dP'_1 \dots dq'_{n-1}\,\dot{q}'_n,$$

when $q'_n = 0$.

But in such a case, as proved in Art. 12, we have

$$dP_1 \dots dq_{n-1}\,\dot{q}_n = dP'_1 \dots dq'_{n-1}\,\dot{q}'_n.$$

So that the total diminution of the number of the m set of molecules in the $P,\ P+dP \dots Q,\ Q+dQ$ state, per unit time, arising from collisions with the n set, will be

$$dP_1 \dots dQ_m \iiint \dots (Ff - F'f')\,dp_1 \dots dq_{n-1}\,\dot{q}_n,$$

where $q_n = q'_n = 0$, that is to say,

$$\frac{dF}{dt}\,dP_1 \dots dQ_m = dP_1 \dots dQ_m \iint \dots (F'f' - Ff)\,dp_1 \dots dq_{n-1}\,\dot{q}_n,$$

$$\therefore \quad \iint \dots \frac{dF}{dt} \log F.\,dP_1 \dots dQ_m = \iint \dots (F'f' - Ff) \log F.\,dP_1 \dots dq_{n-1}\,\dot{q}_n,$$

q_n and q'_n being each equal to zero.

By symmetry

$$\iint \dots \frac{df}{dt} \log f \, dp_1 \dots dq_n = \iint \dots (F'f' - Ff) \log f \, dP_1 \dots dq_{n-1} \dot{q}_n,$$

$$\therefore \iint \dots \frac{dF}{dt} \log F \, dP_1 \dots dQ_m + \iint \dots \frac{df}{dt} \log f \, dp_1 \dots dq_n = \iint \dots (F'f' - Ff) \log Ff \, . \, dP_1 \dots dq_{n-1} \dot{q}_n,$$

where $q_n = q'_n = 0$.

Similarly

$$\iint \dots \frac{dF'}{dt} \log F' \, dP'_1 \dots dQ'_m + \iint \dots \frac{df'}{dt} \log f' \, dp'_1 \dots dq'_n$$

is equal to

$$\iint \dots (Ff - F'f') \log F'f' \, dP'_1 \dots dq'_{n-1} \dot{q}'_n.$$

But since the integral $\iint \dots \frac{dF}{dt} \log F \, dP_1 \dots dQ_m$ extends over all values of each P and Q, including each P' and Q', it follows that

$$\iint \dots \frac{dF}{dt} \log F \, dP_1 \dots dQ_m = \iint \dots \frac{dF'}{dt} \log F' \, dP'_1 \dots dQ'_m,$$

and similarly

$$\iint \dots \frac{df}{dt} \log f \, dp_1 \dots dq_n = \iint \dots \frac{df'}{dt} \log f' \, dp'_1 \dots dq'_n,$$

$$\therefore \iint \dots \frac{dF}{dt} \log F \, dP_1 \dots dQ_m + \iint \dots \frac{df}{dt} \log f \, dp_1 \dots dq_n = \iint \dots (F'f' - Ff) \log Ff \, dP_1 \dots dq_{n-1} \dot{q}_n$$

$$= \iint \dots (Ff - F'f') \log F'f' \, dP_1 \dots dq_{n-1} \dot{q}_n$$

$$= \tfrac{1}{2}\iint \dots (F'f' - Ff) \log \frac{Ff}{F'f'}\, dP_1 \dots dq_{n-1}\, \dot{q}_n,$$

where the argument $(F'f' - Ff) \log \dfrac{Ff}{F'f'}$ is necessarily negative if not zero.

Now let H be taken to represent

$$\iint \dots F(\log F - 1)\, dP_1 \dots dQ_m + \iint \dots f(\log f - 1)\, dp_1 \dots dq_n,$$

then $$\frac{dH}{dt} = \iint \dots \frac{dF}{dt} \log F\, dP_1 \dots dQ_m + \iint \dots \frac{df}{dt} \log f\, dp_1 \dots dq_n,$$

and is therefore essentially negative so far as $\dfrac{dH}{dt}$ depends upon encounters between molecules of the m and n sets, unless the quantities Ff and $F'f'$ are equal to each other, in which case $\dfrac{dH}{dt}$ is zero.

If we had taken H equal to

$$\iint \dots F(P, Q) \{\log F(P, Q) - 1\}\, dP_1 \dots dQ_m + \iint \dots F(p, q) \{\log F(p, q) - 1\}\, dp_1 \dots dq_m,$$

it would have followed by the same reasoning that $\dfrac{dH}{dt}$ was negative unless

$$F(P, Q)\ F(p, q) = F(P', Q')\ F(p', q'),$$

and therefore that $\dfrac{dH}{dt}$ must have been negative unless

$$F(P, Q)\ F(p, q)$$

had been equal to

$$F(P', Q')\ F(p', q'),$$

so far as encounters between pairs of molecules each of the m set were concerned, and similarly for the pairs each of the n set.

And therefore generally, when there are any number of sets of molecules, if the function H be written

$$\Sigma\left\{\iint \dots F(\log F - 1)\, dP_1 \dots dQ_m + \iint \dots f(\log f - 1)\, dp_1 \dots dq_n\right\}$$

for all the forms of F and f in the different sets, the time variation $\frac{dH}{dt}$ will be necessarily negative unless the condition

$$F(P, Q)\, f(p, q) = F(P', Q')\, f(p', q') \quad . \quad . \quad \text{(A)}$$

for every binary encounter combination be satisfied; that is to say, the quantity $\frac{dH}{dt}$ tends to a minimum unless every one of these conditions is separately satisfied whenever encounters take place in the medium, or equation (A) represents a necessary condition of permanence when encounters take place.

In the absence of encounters each of the F's must separately satisfy the condition $\frac{dF}{dt} = 0$, because when there are no encounters

$$F\,.\,dP_1 \dots dQ_n$$

must be independent of the time for each molecule separately.

But the differential product

$$dP_1 \dots dQ_m$$

is known to be independent of the time, and therefore F

must be so. Hence, for permanence we must have for the determination of each form of F the two conditions

$$F(P_1 \dots Q_m) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

independent of the time when no encounters;

$$F(P_1 \dots Q_m)\, f(p_1 \dots q_n) = F(P'_1 \dots Q'_m)\, f(p'_1 \dots q'_n) \quad (2)$$

when there are encounters.

Now the only form of F which can be conceived as satisfying the first condition is $F(E)$, where E is the total energy of the molecule, so that the second condition is reduced to

$$F(E_{P,Q})\, f(E_{p,q}) = F(E_{P',Q'})\, f(E_{p',q'}),$$

where $E_{P,Q} + E_{p,q} = E_{P',Q'} + E_{p',q'}$,

or $F = Ae^{-hE_{P,Q}}$, $f = Be^{-hE_{p,q}}$.

Whence it follows that the e^{-hE} law is both *sufficient* and *necessary* for permanence, provided the system be such that every conceivable arrangement is also an attainable arrangement.

If any restraint be introduced, whereby the attainment of any of the conceivable arrangements is rendered impossible, the reasoning of course fails, if the e^{-hE} arrangement should be included in those thus rendered impossible of attainment, otherwise the e^{-hE} law must still prevail.

15.] From the preceding Article we learn that in the case of a medium composed of sets of molecules such as we have been considering, whatever be the assumed laws of distribution, among the different sets, at any instant, such laws cannot be permanent, unless certain conditions hold amongst them, and that, unless these conditions be satisfied, a certain function H, dependent upon these assumed laws of distribution may be found, which is always, under the action

of encounters, tending to a minimum, and this minimum being attained there is no further tendency to change, or the state is permanent.

The time variation of H, for any assumed laws of distribution, consists, as we have seen, in an integral or sum of a number of terms of the forms

$$\{Ff - F'f'\} \log \frac{F'f'}{Ff} \dot{q}_n,$$

where F and f depend upon the assumed laws of distribution for any given pair of sets with, say, m and n degrees of freedom each, q_n is what may be called an encounter function for two molecules of that pair, $\dot{q}_n$ is the time variation of q_n, and F' and f' are the values of F and f after an encounter.

In thus determining the time variation $\frac{dH}{dt}$ we have limited the investigation to the changes in H from encounters only, because we are considering the question of permanence with distribution laws F, f, &c., and it is clear, *à priori*, that only such distribution laws as make each F and f separately independent of the time need be taken into account, for a distribution law which did not give

$$F . dP_1 \dots dQ_m$$

constant would be clearly inadmissible, and we know that $dP_1 \dots dQ_m$ is constant, therefore F must be so.

Since the H-function, as thus found for any assumed distribution laws, tends under the action of encounters to diminish with the time at a rate which may be determined as above shown, until the distribution laws have arrived at the permanent state, we may find the rate at which the medium starting from any assumed distribution laws, differing from those of the permanent state, tends to approach that state.

As a simple illustration, let us consider a medium like that of Art. 6, consisting of a number of circular disks equal to each other in all respects, with the centre of inertia of each at the distance (c) from the centre of figure, c being small in comparison with the radius of a disk; the notation employed will be the same as that of Art. 6, except that the masses and radii of gyration of all the disks will now be denoted by the same letters.

In this case we know that the law of distribution in the permanent state is

$$A_0 e^{-\frac{M}{2}h_0(u^2+v^2+k^2\omega^2)}\,du\,dv\,d\omega,$$

and we will denote this by $F_0(u,v,\omega)\,du\,dv\,d\omega$ or $F_0\,du\,dv\,d\omega$, and suppose that at any instant the distribution law is $F\,du\,dv\,d\omega$, where

$$F = Ae^{-\frac{M}{2}h(u^2+v^2+\mu k^2\omega^2)}.$$

Let H_0 and H be the H-functions calculated for the respective laws, then we know that

$$H = H_0 + K,$$

where K is some positive quantity which may be called the disturbance, and our object is to find K and $\frac{dK}{dt}$.

Since the total number N of the disks and the total kinetic energy of the medium must be constant, we have the following conditions:

$$A\iiint e^{-\frac{Mh}{2}(u^2+v^2+\mu k^2\omega^2)}\,du\,dv\,d\omega$$

$$= A_0\iiint e^{-\frac{Mh_0}{2}(u^2+v^2+k^2\omega^2)}\,du\,dv\,d\omega = N, \quad (1)$$

$$A\iiint e^{-\frac{Mh}{2}(u^2+v^2+\mu k^2\omega^2)}\,T\,du\,dv\,d\omega$$
$$= A_0\iiint e^{-\frac{Mh_0}{2}(u^2+v^2+k^2\omega^2)}\,T\,du\,dv\,d\omega = N\overline{T}, \quad (2)$$

where $$T = \frac{M}{2}(u^2+v^2+k^2\omega^2),$$

and the bar denotes mean value.

From these equations we get

(1) $$h = \frac{2\mu+1}{3\mu}\,h_0,$$

(2) $$A = \sqrt{\mu}\,k\left(\frac{h}{\pi}\right)^{\frac{3}{2}}N = \sqrt{\mu}\left(\frac{2\mu+1}{3\mu}\right)^{\frac{3}{2}}A_0.$$

Also

$$H = \iiint F(\log F - 1)\,du\,dv\,d\omega = \iiint F\log F\,du\,dv\,d\omega - N$$

$$H_0 = \iiint F_0\log F_0\,du\,dv\,d\omega - N.$$

Therefore

$$K = \iiint F\log F\,du\,dv\,d\omega - \iiint F_0\log F_0\,du\,dv\,d\omega.$$

But $$F = Ae^{-h\left(T+\overline{\mu-1}\,\frac{Mk^2\omega^2}{2}\right)} = Ae^{-hT_1},$$ suppose.

$$\therefore\quad F\log F = Ae^{-hT_1}(\log A - hT_1)$$
$$= Ae^{-hT_1}\left(\log A - h\left(T+\overline{\mu-1}\,\frac{Mk^2\omega^2}{2}\right)\right),$$

$$F_0\log F_0 = A_0\,e^{-h_0 T}(\log A_0 - h_0 T);$$

$$\therefore\quad \iiint F\log F\,du\,dv\,d\omega$$
$$= N\log A - N\overline{hT} - \overline{\mu-1}\,Ah\iiint e^{-hT_1}\,\frac{Mk^2\omega^2}{2}\,du\,dv\,d\omega,$$

$$\iiint F_0 \log F_0 \, du\, dv\, d\omega = N \log A_0 - N h_0 \overline{T}.$$

Therefore

$$K = N \log \frac{A}{A_0} + N(h_0 - h)\,\overline{T} - \overline{\mu - 1}\, Ah \iiint e^{-hT_1} \frac{Mk^2\omega^2}{2}\, du\, dv\, d\omega,$$

$$= N \log \frac{A}{A_0}, \text{ because from integration it follows that}$$

$$N(h_0 - h)\,\overline{T} = \overline{\mu - 1}\, Ah \iiint e^{-hT_1} \frac{Mk^2\omega^2}{2}\, du\, dv\, d\omega.$$

$$\therefore K = N \log \frac{(2\mu + 1)^{\frac{3}{2}}}{3^{\frac{3}{2}}\mu} = N\left\{\frac{(\mu-1)^2}{6} + \text{higher powers of } (\mu - 1)\right\}.$$

In finding $\frac{dK}{dt}$ let us, in the first place, confine our attention to the part of $\frac{dK}{dt}$ arising from collisions of disks whose lines of centres at the instant of collision are parallel to the axis of x.

If s be the diameter of any disk, U and u, V and v, Ω and ω, the respective component translational and rotational velocities at the instant of collision, the number of the required kinds of collisions per unit of time is $(U \sim u)\, 2s$ (see Art. 5), and therefore the part of $\frac{dK}{dt}$ arising from such collisions is equal to

$$\frac{1}{2} \iint \ldots (Ff - F'f') \log \frac{F'f'}{Ff} (U - u)\, 2s\, dU\, dV\, d\Omega\, du\, dv\, d\omega,$$

where the integrations with regard to U and u are to be taken from $u = 0$ to $u = U$, and from $U = 0$ to $U = \infty$.

Also, since in the general expression for $\frac{dK}{dt}$ we are considering all the pairs of disks of which the coordinates of one relative to the other are s and any value of θ from $-\frac{\pi}{2}$ to $+\frac{\pi}{2}$, and in this restricted case only those pairs for which these relative coordinates are s and any value of θ from o to $d\theta$, it is clear that we must replace N^2 in this case by $N^2 \frac{d\theta}{\pi}$, i.e. we must replace A^2 by

$$\frac{N^2 h^3 k^2 \mu}{\pi^2} \cdot \frac{d\theta}{\pi}.$$

Also $$Ff = A^2 e^{-h\left(T+t+\overline{\mu-1}\frac{Mk^2}{2}(\Omega^2+\omega^2)\right)},$$

$$F'f' = A^2 e^{-h\left(T'+t'+\overline{\mu-1}\frac{Mk^2}{2}(\Omega'^2+\omega'^2)\right)},$$

writing T and t for the total kinetic energies of the disks before collision, and T' and t' for the similar quantities after collision;

where $$\Omega' = \Omega - \frac{P}{Mk^2 D}(U-u-p\omega+P\Omega),$$

$$\omega' = \omega + \frac{p}{Mk^2 D}(U-u-p\omega+P\Omega),$$

$$D = \frac{2}{M} + \frac{1}{MK^2}(P^2+p^2);$$

and P and p are perpendiculars from the Centres of Inertia of the respective disks upon their line of centres, and therefore are, at least, of the same order of smallness as (c).

If then c be small we have to a first approximation

$$\Omega' = \Omega - \frac{P}{2k^2}(U-u), \qquad \omega' = \omega + \frac{p}{2k^2}(U-u),$$

and therefore, remembering that $T+t = T'+t'$; and

neglecting c^2, $Ff - F'f'$ is, to the same approximation, equal to

$$A^2 e^{-h\left\{T+t+\overline{\mu-1}\frac{Mk^2}{2}(\Omega^2+\omega^2)\right\}}\left\{1-e^{-\frac{Mh}{2}(\mu-1)(P\Omega-p\omega)(U-u)}\right\}$$

$$= A^2 e^{-h\left\{T+t+\overline{\mu-1}\frac{Mk^2}{2}(\Omega^2+\omega^2)\right\}}\cdot\frac{Mh}{2}(\mu-1)(P\Omega-p\omega)(U-u).$$

Also $$\log(F'f'-Ff) = -\frac{Mh}{2}(\mu-1)(P\Omega-p\omega)(U-u).$$

Therefore to the same approximation $\frac{dK}{dt}$ is equal to

$$-\frac{M^2h^2}{4}A^2(\mu-1)^2 s\iint\ldots e^{-h\left(T+t+\overline{\mu-1}\frac{Mk^2}{2}(\Omega^2+\omega^2)\right)}$$
$$(P\Omega-p\omega)^2(U\sim u)^3\,dU\,du\,dV\,dv\,d\Omega\,d\omega,$$

i.e. to

$$-\frac{M^2h^2}{4}A^2(\mu-1)^2 s\iint\ldots e^{-h\left(T+t+\overline{\mu-1}\frac{Mk^2}{2}(\Omega^2+\omega^2)\right)}$$
$$\overline{P^2}(\Omega^2+\omega^2)(U\sim u)^3\,dU\ldots d\omega,$$

where $\overline{P^2}$ is the mean value of P^2 or p^2, and therefore is of the same order of smallness as c^2.

The result of the integration is clearly of the form

$$\frac{L}{M^2\mu^2h^{\frac{11}{2}}}\cdot\frac{c^2}{k^2},$$

where L is a numerical quantity whose exact value is of no importance to the present investigation.

Therefore the value of this portion of $\frac{dK}{dt}$, remembering that A^2 is here equal to

$$\frac{N^2h^3k^2\mu}{\pi^2}\cdot\frac{d\theta}{\pi},$$

becomes

$$-\frac{CsN^2(\mu-1)^2}{\mu\sqrt{h}}\cdot\frac{c^2}{k^2}\cdot\frac{d\theta}{\pi},$$

and the total value of $\frac{dK}{dt}$ becomes

$$-\frac{CsN^2(\mu-1)^2}{\mu\sqrt{h}}\cdot\frac{c^2}{k^2},$$

C being a known numerical quantity.

Since $K = N\left\{\frac{(\mu-1)^2}{6} + \text{higher powers of } (\mu-1)\right\}$,

we have, if $\mu-1$ be small,

$$\frac{dK}{dt} = -\frac{6CNs}{\sqrt{h_0}}\cdot\frac{c^2}{k^2}\cdot K,$$

$$\text{or} \quad K = K_0 e^{-a\frac{c^2}{k^2}\cdot t},$$

$$\text{where} \quad a = \frac{6CNs}{\sqrt{h_0}}, \quad \text{i.e.} \quad a \propto \frac{Ns}{\sqrt{h_0}}.$$

That is to say, an initial distribution of this nature, in which the mean value of $\frac{Mk^2}{2}\omega^2$ differs from the mean values of $\frac{Mu^2}{2}$ or $\frac{Mv^2}{2}$, will reduce to the permanent distribution at a proportional rate $\frac{ac^2}{k^2}$.

If the original distribution had been represented by either of the laws

$$Ae^{-h\left(T+\mu-1\frac{Mu^2}{2}\right)} \quad \text{or} \quad Ae^{-h\left(T+\mu-1\frac{Mv^2}{2}\right)},$$

that is to say, if it had been a distribution in which the mean values of $\frac{M}{2}u^2$ and $\frac{M}{2}v^2$ had been different from

each other, the value of K would have been the same as before, and the value of $\frac{dK}{dt}$ would also have been the same with the omission of the fraction $\frac{c^2}{k^2}$.

Such a distribution then would, if $\mu - 1$ were small, be represented by a disturbance function which, as in the last case, would have diminished proportionally at the rate $-\alpha$ per unit of time, and therefore with the diminution of $\frac{c}{k}$ the rate of approach to the state of permanence might conceivably be infinitely greater with an initial small inequality between the mean values of the translation component portions of the kinetic energy than it is with an inequality between either of these and the rotation component. And whether the initial disturbance function be great or small we always have its rate of change for a difference in the mean values of $\frac{M}{2} u^2$ and $\frac{M}{2} v^2$ greater than that for a difference in the mean values of $M \frac{k^2 \omega^2}{2}$, and either of the former in a ratio comparable with the ratio $\frac{c^2}{k^2}$.

Mr. Burbury and Professor Tait have, in the Transactions of the Royal Societies of London and Edinburgh, given similar investigations of the rate of subsidence of disturbance in the case of a medium of two sets of elastic spheres, the masses and number of spheres per unit volume of the two sets being M, m and N, n respectively, and the disturbance consisting in an initial small difference between the h constants in the two sets. They have arrived by independent treatment at the result

$$\frac{16}{3\sqrt{\pi}} (N+n) \frac{\sqrt{Mm}}{(M+m)^{\frac{3}{2}}} \cdot \frac{\pi s^2}{\sqrt{h}}$$

for the proportional rate of subsidence, where $\frac{1}{h}$ is the Arithmetic mean of the initial values of the $\frac{1}{h}$ constants.

16.] A number of sets of molecules are moving in a bounded region, taken as unit of volume, as in Art. 13, the masses and number of degrees of freedom of each molecule of any set being denoted by M and m and the number of molecules in the set by N, with suffixes attached to these letters to distinguish different sets; it is required to determine the action of one portion of the medium upon another, or the pressure per unit of surface at any point.

Since the distributions of the molecules of different sets are independent of each other, we will for the present confine our attention to the set denoted by M, m, N, without suffixes.

Suppose that there are dN molecules of the set considered, whose component velocities of translation parallel to the axis of x are between u and $u + du$.

The number of these molecules which cross the elementary area $dy\,dz$ in time dt will be the same as the number of the dN molecules whose centres of inertia are situated within the elementary parallelopiped $dx\,dy\,dz$ in which dx is equal to $u dt$, and this number is

$$dN \,.\, u \,.\, dy\,dz\,dt.$$

Each of these molecules carries across with it a momentum parallel to the axis of x equal to Mu; the total momentum parallel to the axis of x transferred across $dy\,dz$ in the time dt is therefore

$$M\,dN\,u^2\,dy\,dz\,dt.$$

If u be positive this is positive momentum transferred from the negative to the positive side of the plane yz, and if u be negative this is negative momentum similarly transferred from the positive to the negative side of the same plane.

In either case the result is that by the mere motion of these molecules across the area $dydz$ the positive momentum parallel to the axis of x is diminished by the quantity $MdNu^2dydzdt$ on the negative side of the plane yz, and increased by the same quantity on the positive side of that plane in the time dt.

Hence the result is the same as a transference of positive momentum parallel to the axis of x in time dt across the area $dydz$ equal to $Mdydzdt\sum_{-\infty}^{\infty} u^2 dN$, that is equal to

$$dydzdt\,MN\bar{u}^2 \quad \text{or to} \quad dydzdt\,\rho u^2; \quad . \quad . \quad . \quad (a)$$

where ρ is the density of the N set matter at the point x, y, z, and $\bar{u}^2$ is the mean square of the velocities parallel to the axis of x.

But $\bar{u}^2$ is equal to $\frac{\bar{v}^2}{3}$, where $\bar{v}^2$ is the mean square of the velocities of the N set of molecules, and is equal, as we have seen, to $\frac{3}{Mh}$.

Hence there is a transference of positive momentum from the negative to the positive side of the plane yz across the area $dydz$ in the time dt equal to

$$\rho dydzdt\frac{\bar{v}^2}{3}, \text{ or to } \frac{\rho dydzdt}{Mh}.$$

Each separate molecule (whose component velocities of translation are u, v, and w) carries across the same plane momenta parallel to the axis of y and z equal to Mv and Mw respectively, so that in the time dt there are carried across the elementary area $dydz$ momenta parallel to the axes of y and z equal to $\Sigma\overline{Muv}dydzdt$ and $\Sigma\overline{Muw}dydzdt$ respectively.

It is clear from the symmetrical distribution of the velocities that $\Sigma M\overline{uv}$ and $\Sigma M\overline{uw}$ are each equal to zero.

Therefore the resultant mutual action of the two portions of the medium across the elementary area $dydz$ in the time dt is the transference of the momentum $\rho dydzdt\frac{\bar{v}^2}{3}$ parallel to the axis of x across this element from the negative to the positive side.

If this mutual action, or as it is generally called this *pressure*, when referred to unit of surface be denoted by the symbol p, we get the equation

$$pdydzdt = \rho dydzdt \cdot \frac{\bar{v}^2}{3};$$

or

$$p = \rho\frac{\bar{v}^2}{3} = \frac{\rho}{mh}.$$

Since the momenta parallel to y and z remain unaltered, it follows that the mutual action or pressure between portions of the medium separated by any plane is entirely normal to that plane.

Since also the expression for p, or $\rho\frac{\bar{v}^2}{3}$, is independent of the direction of the axis of x, it follows that the pressure at any point of the medium is the same in all directions.

If we suppose the contiguous portions of the medium to be separated by a material instead of an ideal plane, it will clearly be necessary for the maintenance of the equilibrium that there should be an action between this plane and the adjacent portion of the medium exactly equivalent to the transference of momenta estimated above. Hence the pressure or force between the plane and medium is normal to the plane, and its value per unit of time and surface is $\frac{\rho}{mh}$ at any point. And this value remains unaffected by

turning the plane of separation in any direction about the point.*

When several different sets of molecules are present together in the region under consideration, if ρ_1, ρ_2, &c. be the densities of the matter of the different sets in the neighbourhood of the point x, y, z, and if p_1, p_2, &c. be the pressures at that point, defined as above, of the media composed of these different sets, and if M_1, M_2, &c. be the masses of the individual molecules of each of the sets, and p the total pressure, we shall have

$$p = p_1 + p_2 + \&c. = \frac{1}{h} \Sigma \frac{\rho}{M}.$$

17.] We may prove that the value of p as determined in the last Article satisfies the necessary condition of equilibrium of the medium.

For consider the elementary parallelopiped $dxdydz$ situated in the neighbourhood of the point x, y, z.

The positive momentum of the N set of molecule matter within this element parallel to x is, as we have seen, increased by the quantity $pdydzdt$ in the time dt by transference of matter across the face $dydz$ nearer to the plane of yz, or, as we may call it, the left-hand face, and the x momentum is in the same time diminished by the quantity $\left(p + \frac{dp}{dx} dx\right) dydzdt$ by transference across the right-hand

* It is important to distinguish between the velocity of agitation of the molecules treated of in the preceding reasoning and that which we are accustomed to consider as the velocity of the medium itself. This latter velocity has been defined by Professor Clerk Maxwell as follows. If we determine the motion of the centre of gravity of all the molecules within a very small region surrounding a point in a medium, then the velocity of the medium within that region is defined as the velocity of the centre of gravity of all the molecules within that region. Should such a velocity exist in the medium under consideration, we must suppose that our ideal plane of separation moves with the same velocity, and therefore that the number of molecules crossing it in any direction is on the average equal to the number crossing it in the exactly opposite direction.

face. On the whole, therefore, the positive x momentum within the element is diminished by the quantity $\frac{dp}{dx}\,dydzdxdt$ in the time dt.

It is necessary therefore for the permanent state of the medium that the impressed force on the N molecule matter within the element should produce a resultant momentum, equal to the last found quantity, in the time dt, that is to say, we should have

$$\frac{dp}{dx} = \rho \overline{X},$$

where $\overline{X}$ is the mean value of the x force on all the molecules whose centres of inertia lie within $dxdydz$.

Now the number of the N set molecules whose m momenta and m coordinates lie between

$$p_1 \text{ and } p_1 + dp_1 \ldots p_m \text{ and } p_m + dp_m,$$
$$q_1 \text{ and } q_1 + dq_1 \ldots q_m \text{ and } q_m + dq_m,$$

is of the form

$$Ae^{-h(\chi+T)}\,dp_1 \ldots dq_m.$$

Let the coordinates be the x, y, z of the centre of inertia and $q_4 \ldots q_m$, then the whole number whose centre of inertia lie within the parallelopiped $dxdydz$ is

$$A\,dxdydz \iiint \ldots e^{-h(\chi+T)}\,dp_1 \ldots dp_m\,dq_4 \ldots dq_m,$$

and therefore the density ρ at the point x, y, z is of the form

$$A \iiint \ldots e^{-h(\chi+T)}\,dp_1 \ldots dp_m\,dq_4 \ldots dq_m,$$

and

$$\frac{d\rho}{dx} \text{ is } -hA \iiint \ldots \frac{d\chi}{dx}\,e^{-h(\chi+T)}\,dp_1 \ldots dp_m\,dq_4 \ldots dq_m.$$

Since T is equal to

$$\frac{M}{2}(u^2+v^2+w^2)+f(p_4 \dots p_m, q_4 \dots q_m)$$

and is therefore independent of x, y and z,

or $\frac{d\rho}{dx}$ is $-hA\frac{d\overline{X}}{dx}\int\int \dots e^{-h(\chi+T)}\, dp_1 \dots dp_m\, dq_2 \dots dq_m$

$$= Mh\rho\overline{X},$$

where $\overline{X}$ is the mean value of the x force on the molecules within $dx\,dy\,dz$ for all values of the momenta and relative coordinates of these molecules.

Therefore $$\frac{dp}{dx} = \frac{1}{Mh}\frac{d\rho}{dx} = \rho\overline{X}.$$

18.] In the determination of p in Article 17 we have only considered the transference of momentum which would have taken place across the plane of separation owing to the motion of separate molecules; that is to say, supposing one portion of the medium to be separated from the other by a material boundary, the value of p already found is that arising from the bombardment of the boundary by the separately impinging molecules and assumes that the time any one molecule is in collision with any other during any measurable interval is so small as to be negligible; when this condition is not satisfied, owing either to molecular density or the minimum irreducible volume of separate molecules, a correction is required; to find this we must prove the following propositions due to Clausius.

When any number of material particles are in motion within a limited space so that the particles do not move continually further and further from their original positions, and provided also that the velocities of each particle do not continually increase or decrease, such a system of material particles is said to be in *stationary motion.*

If X, Y, Z be the component forces upon any one of a system of particles in stationary motion, and x, y, and z be the coordinates of such particle referred to any origin and axes, and the quantity $Xx+Yy+Zz$ be found for such particle, then the mean value of the expression

$$-\tfrac{1}{2}\Sigma(Xx+Yy+Zz)$$

during any period of stationary motion of the system, where Σ represents summation for all the particles, is called the *Virial* of the system.

When a system of material particles is in stationary motion the mean kinetic energy of the system is equal to its virial.

If x be any function of t,

$$\frac{d^2}{dt^2}(x^2) = 2\frac{d}{dt}\cdot\left(x\frac{dx}{dt}\right) = 2\left(\frac{dx}{dt}\right)^2 + 2x\frac{d^2x}{dt^2};$$

$$\therefore \quad 2\left(\frac{dx}{dt}\right)^2 = -2x\frac{d^2x}{dt^2} + \frac{d^2}{dt^2}(x^2). \quad . \quad . \quad (a)$$

Let x be the coordinate parallel to the axis of x at the time t of that one of the material particles whose mass is M, and let X be the component force on that particle parallel to the same axis, then

$$M\frac{d^2x}{dt^2} = X.$$

Hence equation (a) gives us

$$\frac{M}{2}\left(\frac{dx}{dt}\right)^2 = -\frac{Xx}{2} + \frac{M}{4}\cdot\frac{d^2}{dt^2}(x^2),$$

$$\therefore \frac{M}{2t}\cdot\int_0^t\left(\frac{dx}{dt}\right)^2 dt = -\frac{1}{2t}\cdot\int_0^t Xx\,dt + \frac{M}{4t}\cdot\left[\frac{d(x^2)}{dt} - \left[\frac{d(x^2)}{dt}\right]_0\right],$$

where $\left[\frac{d(x^2)}{dt}\right]_0$ denotes the initial value of $\frac{d(x^2)}{dt}$.

Now $\frac{1}{t}\cdot\int_0^t\left(\frac{dx}{dt}\right)^2 dt$ and $\frac{1}{t}\cdot\int_0^t Xx\,dt$ are the mean values of $\left(\frac{dx}{dt}\right)^2$ and Xx during the time t.

If the motion be strictly periodic and t be taken equal to the length of a period or any multiple whatever of that length, then the last term on the right-hand side becomes zero; and if the motion be not strictly periodic, still from its stationary character as above defined, although the coefficient of $\frac{M}{4t}$ in the last term does not necessarily become zero for all values of t however large, yet its value cannot increase indefinitely, but can only fluctuate within certain limits, and therefore by sufficiently increasing the value of t the last term on the right-hand side becomes inappreciable and may be neglected, so that we obtain, in either case, the equation

$$\frac{M}{2}\cdot\overline{\left(\frac{dx}{dt}\right)^2} = -\tfrac{1}{2}\,\overline{Xx};$$

and therefore by similar reasoning with respect to y and z, Y and Z,

$$\frac{M}{2}\cdot\overline{\left[\left(\frac{dx}{dt}\right)^2+\left(\frac{dy}{dt}\right)^2+\left(\frac{dz}{dt}\right)^2\right]} = -\tfrac{1}{2}\,\overline{(Xx+Yy+Zz)},$$

or
$$\frac{M}{2}\cdot\overline{v^2} = -\tfrac{1}{2}\,\overline{(Xx+Yy+Zz)};$$

and therefore for any system of particles,

$$\Sigma\,\frac{M}{2}\cdot\overline{v^2} = -\tfrac{1}{2}\,\Sigma\,\overline{(Xx+Yy+Zz)}.$$

19.] Any number of particles being in motion in a given region, to find the pressure referred to unit of surface at any

point within the medium, supposing the particles to be acted on by fixed-central forces, and mutual forces between the particles, any functions of the distance between them, and which become infinitely large with the infinite diminution of this distance.

Let O be the point in question, and about O describe a closed surface S of simple continuity, and take O for the origin of coordinates.

If the mutual action between the adjacent particles within and without S be replaced by a force pdS acting normally at every element dS, the distribution as to momenta and coordinates of the molecules now confined within S will, on the average of any finite time, be the same as in the actual case.

Now by the virial proposition, if M be the mass and $\bar{v}^2$ the mean square velocity of any particle within S; X, Y, Z the components of the moving forces on that particle, and x, y, z its coordinates,

$$\Sigma \frac{M\bar{v}^2}{2} = -\tfrac{1}{2}\Sigma\overline{(Xx+Yy+Zz)},$$

the bar denoting mean values.

The part of the second term arising from pressure forces on the surface element dS is

$$-\tfrac{1}{2}pdS(x\cos\alpha + y\cos\beta + z\cos\gamma),$$

where α, β, γ are the angles between the axes and the normal at dS drawn inwards.

Therefore if ϖ be the perpendicular from O upon the element dS, the portion of the pressure virial contributed by the element dS becomes

$$\tfrac{1}{2}p\varpi dS,$$

and the virial equation becomes, therefore,

$$\Sigma p\varpi dS = \Sigma M\bar{v}^2 + \Sigma\overline{(Xx+Yy+Zz)},$$

or if V be the volume included within S, and dV the elementary pyramidal volume with base dS and vertex O,

$$3\Sigma(pdV) = \Sigma M\bar{v}^2 + \Sigma(\overline{Xx+Yy+Zz}).$$

If S, and therefore V, be indefinitely diminished, we get for the value of p at the point O, being the value sought,

$$p = \frac{\rho\bar{v}^2}{3} + \frac{1}{3}\,lt_{V=0}\frac{\Sigma(\overline{Xx+Yy+Zz})}{V}.$$

The forces X, Y, Z include all the forces in the field except the pressure forces, but since x, y, z become infinitely small with the indefinite diminution of V it follows that all the terms in $Xx+Yy+Zz$ except those arising from infinitely large values of X, Y, Z may be neglected, and therefore that the only terms in $Xx+Yy+Zz$ to be retained are those arising from the infinitely large mutual forces of the particles within S.

Now if x', y', z' and x'', y'', z'' be the coordinates of two particles M' and M'', and if R be the mutual moving force, and r the distance between M' and M'', we have

$$X' = -R\frac{x''-x'}{r}, \quad X'' = R\frac{x''-x'}{r},$$

R being positive when repulsive, with corresponding values for the other components; so that

$$X'x' + Y'y' + Z'z' + X''x'' + Y''y'' + Z''z''$$

becomes $$\frac{R}{r}\cdot\{(x''-x')^2+(y''-y')^2+(z''-z')^2\},$$

or $$Rr,$$

with similar results for all other pairs, and the value of p at O is therefore given by the equation

$$p = \frac{\rho\bar{v}^2}{3} + lt_{V=0}\,\Sigma\Sigma\frac{Rr}{l},$$

the $\Sigma\Sigma$ denoting summation for every pair of particles within V.

If the particles be replaced by molecules with irreducible minimum volume, the equation

$$\Sigma p \varpi dS = \Sigma m\bar{v}^2 + \Sigma(\overline{Xx + Yy + Zz})$$

still holds as before, where X, Y, Z are the components of the resultant force on each molecule, and the molecule is replaced by a particle, of equal mass, at its centre of inertia, but the direction of the mutual force between two molecules does not generally lie accurately in the line joining their centres of inertia. Since the dimensions of the molecules are very small, this deviation is unimportant for a pair at any measurable distance from each other, but it is otherwise for contiguous or nearly contiguous molecules. Hence the substitution of $\Sigma\Sigma(Rr)$ for $\Sigma(Xx + Yy + Zz)$ for the molecules within the small volume V is inadmissible, except indeed for spherical molecules.

We must remember also that in passing from material particles, or Boskovichian atoms, to molecules such as they are generally conceived, namely with an irreducible minimum volume however small, the indefinite diminution of the volume of S is unattainable without destroying the hypothesis of many mutually acting molecules being comprised within S.

In the case of such molecules, therefore, we may continue to use the equation

$$p = \frac{\rho\bar{v}^2}{3} + \frac{1}{3}lt_{V=0}\,\Sigma\Sigma\frac{Rr}{V}$$

for the determination of p, although we cannot give an accurate mathematical meaning to the second term in the right-hand side; $\Sigma(Rr)$ standing for $\Sigma(Xx + Yy + Zz)$.*

* This is the same difficulty as that alluded to in the introduction as occurring in the definition of density at any point in a medium of molecules with irreducible minimum volume.

If, for example, as will always be the case, in any medium to which our reasoning is applicable, the irreducible minimum volume of a molecule be quite inappreciable in comparison with any measurable volume however small, then the expression $\frac{\Sigma\Sigma(\overline{Rr})}{V}$ may be regarded as the ratio of the Rr products for all pairs of molecules, within a sphere about O, of extremely small measurable radius, to the volume of that sphere.

If our molecules, for instance, were hard elastic spheres, each of mass M and radius s, and if N were the number of these spheres contained within the small sphere about O, then, remembering that R and r at each encounter are Mu and $2s$ respectively, where u is the relative velocity in the line of centres, it follows from the reasoning of Art. 5 that, omitting certain finite numerical factors, $\Sigma\Sigma(\overline{Rr})$ would be

$$\frac{N^2 M s^3}{V}\bar{v}^2,$$

and therefore $lt_{V=0}\frac{\Sigma\Sigma\overline{Rr}}{V}$ would in this case be, with similar omission,

$$lt_{V=0}\frac{NM}{V}\cdot\frac{Ns^3}{V}\bar{v}^2,$$

or $$\rho\bar{v}^2 . lt_{V=0}\frac{\text{total volume of inclosed spheres}}{V}.$$

In such a case, therefore, the second term in the value of p vanishes in comparison with the first term, whenever, owing either to the smallness of the individual molecules or the smallness of the number of such molecules per unit of volume in the neighbourhood of the point O, the total minimum irreducible volume of the molecules per unit volume near that point is very small, and therefore in either

of these cases the value of p is sensibly reduced to the first term, or

$$p = \frac{\rho \bar{v}^2}{3}.$$

But, on either of the last-mentioned assumptions, the $e^{-h(\chi+T)}$ law of distribution has been established for a field of fixed central forces, and therefore by Art. 17 the necessary condition of equilibrium

$$\frac{dp}{dx} = \rho X$$

also holds.

When neither one nor the other of the aforesaid assumptions is satisfied, we get

$$p = \frac{\rho \bar{v}^2}{3} + \frac{1}{3} lt_{V=0} \frac{\Sigma\Sigma Rr}{V},$$

which would not satisfy the condition

$$\frac{dp}{dx} = \rho X$$

if the $e^{-h(\chi+T)}$ law held good.

But, unless either of these assumptions hold, the $e^{-h(\chi+T)}$ law has not been established, we conclude therefore that this law of distribution is a necessary and sufficient condition of permanence for a medium of spherical molecules in a field of fixed central forces on either of these assumptions, (1) that either the number of molecules in unit volume, i.e. the molecule density, is very small; (2) that the molecules themselves are so small as to be practically material points or Boskovichian atoms.

So far as these conditions are not fulfilled the $e^{-h(\chi+T)}$ law must be regarded as approximate, the more correct statement of it being possibly of the form

$$e^{-h\{E+\mu\phi(E)\}},$$

where E is $\chi + T$, ϕ some function, and μ a small function of x, y, z, whose difference from zero depends upon the extent of the departure from the aforesaid conditions.

The evaluation of $\Sigma\Sigma(Rr)$ for spherical molecules in the above investigation proceeds on the assumption that the distribution is uniform throughout the volume V when V is very much diminished. Should the law of distribution lead to a very rapid space variation of the density at any point in the medium the reasoning is, so far, precarious.

It may be assumed that the results arrived at for hard elastic spherical molecules hold good substantially for molecules of any shape and constitution whatever.

20.] Hitherto we have confined our attention to elastic molecules moving in a field of central forces, in which, therefore, the potential at every point is a determinate function of the coordinates of that point the same for all times.

In such a case, viewing the problem under the ordinary conventional aspect, we say that there are no forces in the field except those from fixed centres, and no potential except that of the fixed central forces.

But the truer view would be, as already mentioned in Art. 12 above, to regard the molecules as subject to mutual forces, in addition to those from fixed centres, infinitely great during their action, but acting in each case during intervals of time so very small that in any measureable length of time their average potential is absolutely inappreciable in comparison with that of the fixed centre forces, so that the χ of the above-mentioned law at any point is still the χ at that point of the fixed central forces only.

The treatment of the problem under this aspect is given above in Art. 12, where the collision is replaced by the encounter, that is to say, an exceptional action of forces between the molecules lasting for a short but not absolutely evanescent interval of time, and not inconsistent

with changes of the coordinates defining the position, but still subject to the condition that the chance of any molecule being in encounter simultaneously with more than one other molecule is infinitely small, and therefore that the average potential of such encounter forces during any finite interval of time is evanescent.

Such encounter forces, on the supposition of spherical molecules, must clearly be of some such form as $\frac{\mu}{(r-s)^\nu}$, where r is the distance between the centres, s the sum of their radii, and ν a very large number, and indeed it is under this aspect that the evaluation of the term $\frac{\Sigma\Sigma Rr}{V}$ in Article 19 has been performed.

Now suppose that (the molecules being still for the moment regarded as hard elastic spheres) there were mutual forces between them of the form $\frac{\mu}{r^2}$, $\frac{\mu}{r^3}$, &c., where r is the distance between the centres and the indices of r in the denominators are not infinitely great, then the potential at any point P of the field would not be a determinate function of the position of P, owing to the motion of the molecules, but, if a permanent distribution were attained, the potential at P of molecules remote from P would not be sensibly affected by their motion but would be, like that of the fixed central forces, a function of the distance only, while the potential of the particles near to P would depend upon the shifting positions of these particles and would vary from time to time. In fact, if the μ in the case of each of these forces were very small, a distance b might be conceived; it may be much greater than the radius a of each sphere, but yet much smaller than any measurable quantity, such that for two spheres whose central distance was greater than b the mutual action was

absolutely negligible, and the potential at P of the infinitely great number of spheres lying outside the sphere of radius b described about P would have a value dependent upon the permanent distribution but independent of the time, while that of the spheres lying within the b sphere would vary with the motion of such included spheres; in point of fact all the spheres lying within the b sphere would be in an encounter with the spheres with centre at P and with one another, in a field of practically fixed centre forces arising from the given fixed centre forces and the sensibly fixed centre forces of the spheres external to the b spheres.

If the medium density were so small that the chance of more than two spheres being simultaneously in such encounter was infinitely less than the chance of a binary encounter, it would follow from the reasoning of Art. 12 that the $e^{-h(\chi+T)}$ law was a necessary and sufficient condition of permanent distribution, where χ includes the potential of all the given fixed central forces at any point and also the given fixed central forces arising from molecules external to the b sphere about that point.

If the volume of a sphere of radius $\frac{b}{2}$ described round each spherical molecule and concentric with it were called the *effective volume* of that sphere, the condition as above enunciated would obviously be, that the number of spheres in unit volume or the effective volume of each sphere must be so small that the total of the effective volumes per unit of volume was a very small fraction.

When this condition is satisfied it may be shown, much as in the case of the hard elastic spheres, that $lt_{V=0} \frac{\Sigma\Sigma R\bar{r}}{3V}$ is insensible compared with $\frac{\rho\bar{v}^2}{3}$, provided the additional condition of the preponderance of kinetic over potential

energy be maintained. The restrictions as to the number and masses of the molecules thus introduced would necessitate the part of χ, depending upon intermolecular forces, being very small and indeed absolutely evanescent for values of λ greater than 2 or 3.

The reasoning may obviously be extended to molecules other than spherical and with any number of degrees of freedom. In this more general case there may be interatomic forces whose potential must also be included in the application of the $e^{-h(\chi+T)}$ law, but such forces do not enter into the term $\Sigma\Sigma(\overline{Rr})$, or more correctly $\Sigma(\overline{Xx}+\overline{Yy}+\overline{Zz})$.

21.] If any number of sets of molecules are inclosed in a region under the circumstances of the preceding Articles, to find the work done by the expansion of the medium, uniformly in all directions, i.e. the increase of every linear dimension bearing the same ratio to the original length of that dimension.

Suppose that there is in the first place only one set of molecules N in number, the mass of each being M and its number of degrees of freedom being m, and suppose that the force field is that of given fixed central and intermolecular forces.

If there are no fixed central forces the pressure p, at every point of the bounding surface, is the same, and the required work (dW) is equal therefore to pdV.

But in this case, as just now proved, we have

$$pV = \tfrac{1}{3}\Sigma M\bar{v}^2 + \tfrac{1}{3}\Sigma(\overline{Rr}),$$

supposing each intermolecular force R to be positive when it acts repulsively.

Therefore

$$dW = pdV = \frac{dV}{3V}\Sigma_m \bar{v}^2 + \frac{dV}{3V}\Sigma(\overline{Rr}),$$

but since linear expansion is $\frac{1}{3}$rd of cubical expansion, we have $\frac{dV}{3V} = \frac{dr}{r}$, where r is any linear dimension.

Therefore, in this case,

$$dW = \frac{dV}{3V} \cdot N\bar{v}^2 + \Sigma\left(\overline{Rr \cdot \frac{dr}{r}}\right)$$

$$= \frac{dV}{3V} N\bar{v}^2 + \Sigma\,\overline{R\,dr}$$

$$= \frac{dV}{V} \cdot \frac{N}{h} - \overline{\frac{d\chi}{dV}}\, dV;$$

where $\overline{\frac{d\chi}{dV}}$ is the mean value of $\frac{d\chi}{dV}$, and to be carefully distinguished from $\frac{d}{dV}\bar{\chi}$.*

If, however, there be external forces, and p therefore be not constant over the surface, then we must use the equation

$$\Sigma\, p\varpi\, dS = \Sigma\, M\bar{v}^2 + \Sigma\,\overline{(Xx + Yy + Zz)}.$$

If μ be the ratio of the increase of each linear dimension to the original length of that dimension, which is constant throughout and equal to $\frac{dV}{3V}$, our equation becomes

$$\Sigma\, p\mu\varpi\, dS = \mu\Sigma\, M\bar{v}^2 + \Sigma\,\overline{(X\mu x + Y\mu y + Z\mu z)},$$

i.e. $$\Sigma\, p\, d\varpi\, dS = \frac{dV}{3V} \cdot \Sigma\, M\bar{v}^2 + \Sigma\,(Xdx + Ydy + Zdz),$$

or $$dW = \frac{dV}{V} \cdot \frac{N}{h} - \overline{\frac{d\chi}{dV}}\, dV,$$

as before.

* See also a paper by Mr. S. H. Burbury, F.R.S., published in the Philosophical Magazine, January, 1876.

The change of potential of interatomic forces is not considered in this investigation, so that $\frac{d\overline{\chi}}{dV}$ refers only to the intermolecular forces.

For there is no necessary connection between molecular expansion and contraction and the expansion and contraction of the whole volume, and therefore on the average the loss and gain of interatomic potential may be regarded as balancing each other.

22.] A number of sets of molecules are in a given region of space under the circumstances of previous Articles, the field of force being perfectly unrestricted and including interatomic, fixed-central, and intermolecular forces; then, if an increase of Energy equal to δQ be imparted to the medium, there exists a function ϕ such that

$$h\,\delta Q = \delta\phi,$$

or $h\,\delta Q$ is a perfect differential provided the e^{-hE} law hold good.

Suppose, in the first place, that the molecules are all of one set, each with m degrees of freedom, and that there are N of them.

When any molecule has its momenta and coordinates between p_1 and $p_1+dp_1 \ldots q_m$ and q_m+dq_m, let that molecule be said to be in the A_1 state, and for different corresponding limits of the variables let it be said to be in the A_2, A_3, &c. states respectively. Let the product of the differentials of the m momenta in the A_1, A_2, &c. states be denoted by ds_1, ds_2, &c., and let the corresponding products for the coordinates be denoted by $d\sigma_1$, $d\sigma_2$, &c. And let also the potential and kinetic energies for these states be χ_1, χ_2, &c., T_1, T_2, &c.

Then, since the number of molecules of this set in the A_1 state is proportional to $e^{-h(\chi_1+T_1)}\,ds_1\,d\sigma_1$ with similar ex-

pressions for other molecules, it will follow that the chance of the first of the N molecules in the medium considered being in the A_1 state in any length of time is also proportional to $e^{-h(\chi_1+T_1)}\,ds_1\,d\sigma_1$ with similar expressions for the 2nd, 3rd, &c. molecules being in the states A_2, A_3, &c., provided always the total volumes of the N molecules be inconsiderable in comparison with the whole volume of the containing region, because if this proviso be not satisfied we cannot regard the aforesaid chances as independent. Subject therefore to this proviso, it will follow that the chance of the N molecules being in the $A_1, A_2 \ldots A_N$ states respectively at any instant will be

$$Ce^{-h(\chi+T)}\,dx_1 \ldots dz_N\,ds\,d\sigma,$$

where χ and T are the total Energies, Potential and Kinetic, of all the molecules, ds being the product of all the momenta differentials $dp_1 \ldots dp_{mN}$ contained in $ds_1 \ldots ds_N$ above, and $d\sigma$ the product of all the coordinate differentials in $d\sigma_1 \ldots d\sigma_N$ above, except the $3N$ differentials $dx_1 \ldots dz_N$; integrating therefore for all the momenta, we have the chance that the Nm coordinates are between

$$x_1,\ x_1+dx_1 \ldots z_N,\ z_N+dz_N,$$

$$q_{4,1},\ q_{4,1}+dq_{4,1} \ldots q_{m,N},\ q_{m,N}+dq_{m,N},$$

equal to $$Pe^{-h\chi}\,d\sigma dx_1 \ldots dz_N,$$

where P is a function of all the mN coordinates except the $3N$ coordinates $x_1 \ldots z_N$, and $d\sigma$ is the product of these remaining $(m-3)N$ coordinates.

Hence it follows that the mean value, $\bar{f}$, of any function f of the position of the molecules, will be determined by the equation

$$\bar{f} = \frac{\iiint \ldots f P e^{-h\chi}\,d\sigma\,dx_1 \ldots dz_N}{\iiint \ldots P e^{-h\chi}\,d\sigma\,dx_1 \ldots dz_N}.$$

Suppose now that a small increase of energy δQ is imparted to this medium of molecules, then h and V will, in general, vary. Let their increments be denoted by δh and δV respectively.

The imparted energy δQ will be equal to

$$\delta \overline{T} + \delta \bar{\chi} + \delta \overline{W},$$

where $\overline{T}$, $\bar{\chi}$ and $\overline{W}$ are the mean values of the kinetic and potential energies of the medium and the work done by expansion.

Now $$\delta \overline{T} = \frac{\delta (mN)}{2h} = -\frac{mN}{2h^2}\delta h,$$

and $$\delta \overline{W} = \frac{N}{h}\cdot\frac{\delta V}{V} - \frac{\overline{\delta \chi}}{\delta V}\delta V, \quad \text{by last article.}$$

$$\therefore \quad h\delta Q = -\frac{mN}{2h}\delta h + h\overline{\delta\chi} + N\frac{\delta V}{V} - h\frac{\overline{\delta\chi}}{\delta V}.\delta V. \quad . \quad (A)$$

Now let $$u = \log\left(\iiint \dots Pe^{-h\chi}\, d\sigma\, dx_1 \dots dz_N\right),$$

then

$$\frac{du}{dh}\delta h = -\frac{\iiint \dots \chi Pe^{-h\chi}\, d\sigma\, dx_1 \dots dz_N}{\iiint \dots Pe^{-h\chi}\, d\sigma\, dx_1 \dots dz_N}\delta h = -\bar{\chi}\,\delta h.$$

Also

$$\frac{du}{dV}\delta V = -h\frac{\iiint \dots \frac{d\chi}{dV} Pe^{-h\chi}\, d\sigma\, dx_1 \dots dz_N}{\iiint \dots Pe^{-h\chi}\, d\sigma\, dx_1 \dots dz_N}\delta V$$

$$+\frac{\iiint \dots Pe^{-h\chi}\, d\sigma\, \delta(dx_1 \dots dz_N)}{\iiint \dots Pe^{-h\chi}\, d\sigma\, dx_1 \dots dz_N},$$

where $\delta(dx_1 \dots dz_N)$ is the increase of the differential product arising from the increase δV of V.

So that $$\delta . dx_1 = \frac{\delta V}{3V} dx_1,$$

and

$$\delta(dx_1 \dots dz_N) = dx_2 \dots dz_N \delta\, dx_1 + dx_1 \dots dz_N \delta\, dx_2 + \&c. \text{ to } 3N \text{ terms}$$

$$= N \frac{\delta V}{V} . dx_1 \dots dz_N.$$

Whence $$\frac{du}{dV} . dV = -h \frac{d\bar{\chi}}{dV} \delta V + N \frac{\delta V}{V}.$$

Substituting in (A) we have, therefore,

$$h\delta Q = -\frac{mN}{2h} \delta h + h \delta \bar{\chi} + \bar{\chi} \delta h + \delta u$$

$$= \delta \left\{ -\frac{mN}{2} \log h + h\bar{\chi} + \log \iiint \dots Pe^{-h\chi} d\sigma\, dx_1 \dots dz_N \right\}.$$

If there be any number of sets of molecules we have, since the distribution of each set is independent of the distributions of all the rest,

$$h\delta Q = \delta \Sigma \left\{ -\frac{mN}{2} \log h + h\bar{\chi} + \log \iiint \dots Pe^{-h\chi} d\sigma\, dx_1 \dots dz_N \right\},$$

Σ denoting summation for all values of m and N.

23.] We now proceed to summarise the results at which we have arrived, concerning the physical properties of a medium of sets of molecules moving about in a region of space very much larger than the sum of the irreducible minimum volumes of the molecules, and acted on by fixed central and interatomic forces only.

On such a supposition the term $lt_{V=0} \frac{\Sigma\Sigma\, Rr}{V}$ disappears from the value p, and there is no work done by or upon any of the forces, except fixed central forces, on expansion or compression of the medium, and the following physical

properties of the medium have been proved to hold in a state of permanent or stationary motion.

In the first place, we have proved that there is one quantity which is the same for every set, namely, the mean kinetic energy of translation of each of the molecules, or $\frac{3}{2h}$. Let this quantity be called τ.

In the second place, we have found that the distributions of the molecules of each set, both as to momenta and position, is independent of the co-existence of the molecules of the remaining sets, and is in all the same as if that particular set alone existed in the region considered.

We have also found that if p be the pressure referred to unit of surface at any point in the medium on any imaginary material surface drawn through the point, ρ the density at that point, and therefore $\frac{\rho}{M}$ the molecular density, (M being the mass of each molecule of the set considered), then

$$p = \frac{2}{3M}\rho\tau,$$

an equation which expresses these third and fourth properties of the medium; viz.,

Third, that when the mean kinetic energy of translation remains constant the pressures varies directly as the density; and Fourth, when the density remains constant the pressure varies as the mean kinetic energy of translation.

Fifth, we see from the value of p that whenever two media composed of sets of different molecules are so related that the pressure referred to unit of surface and the mean kinetic energy of translation are the same in both media, then the molecular densities are also the same in both media.

If now we compare these results with the accepted

properties of an ideal perfect gas at rest, or of a mixture of such gases, we know—

First, that there is one physical property, viz. the temperature, which must be the same for each gas at each point.

Second, from the law of Dalton, that the pressure and density of each gas at every point must be the same as if the other gases did not exist, or that each gas acts as a vacuum to all the rest.

Third, from Boyle's law, that so long as the temperature remains the same the pressure is proportional to the density.

Fourth, from Charles's and Gay Lussac's law, that when the temperature and density both vary, the pressure varies as the absolute temperature and the density conjointly.

Fifth, from Gay Lussac's law, that when two gases are at the same pressure and temperature their atomic densities are the same.

In these five particulars therefore, generally recognised as summarising the physical properties of the ideal perfect gas, if we replace the terms mean kinetic energy of translation and molecule, by absolute temperature and chemical atom respectively, the physical properties of the moving molecular medium become absolutely identical with those of the ideal perfect gas.

In both cases, also, there is no change of potential energy by expansion or contraction, and in both cases the known thermodynamical law

$$\frac{dQ}{\tau} = d\phi$$

is established, the term equilibrium in the case of the medium being interpreted as stationary motion or permanence of distribution.*

* The student will find little difficulty in proving the equation

$$\delta Q = N\delta\tau + \delta\int\left(\tau\frac{dp}{d\tau} - p\right)dv + p\,\delta v,$$

a well-known equation in thermodynamics.

The physical laws as above stated are generally regarded as those of ideal perfect gases, although they are not quite accurately satisfied by any gases actually existing. They represent only limiting states to which actual gases approach more closely as they more nearly correspond to perfect gases.

For example, there is, in all actual gases, a slight departure from the laws of Boyle and Charles or Gay Lussac, and there is also always a slight indication of change of potential energy on compression or expansion; and just so in the molecular medium, unless either the molecular density N, or else the irreducible molecular volume were so extremely small as to ensure the vanishing of the $\frac{\Sigma\Sigma Rr}{V}$ term, the $e^{-h(\alpha+T)}$ distribution is not rigorously proved, nor the $p = k\rho\tau$ equation established. It would appear therefore that up to this point we are in a position to infer with very great confidence that a perfect gas, if such exists, is accurately represented by a moving molecular medium in the limiting state above indicated, and that all gases are represented by a molecular medium nearly approaching to that limiting state.*

24.] There is one physical property, however, in which this agreement is not so complete, and this we proceed to consider.

A homogeneous perfect gas being supposed to be constituted of moving molecules with any given number of degrees of freedom, required to find the ratio of the specific heat at constant pressure to that at constant volume.

First suppose that when a small quantity δQ of heat is

* It appears from Art. 20 that the e^{-hE} law of distribution might prevail when there are sensible intermolecular forces in the medium, and therefore sensible gain or loss of potential Energy on compression or expansion. Gases represented by such media would obey the five gaseous laws above mentioned, even though their Energy were not entirely Kinetic.

imparted to a unit of mass of the gas the temperature is raised from τ to $\tau+\delta\tau$, the volume remaining constant.

Since the volume remains unchanged there is no external work performed, and therefore the whole of this energy δQ must be accounted for by increase of the total kinetic energy and of the potential energy, therefore

$$\delta Q = N(\delta\tau + \delta\chi),$$

where $\delta\tau$ and $\delta\chi$ are the increases of mean total kinetic and potential energy respectively of any molecule, and N is the number of molecules in the unit of mass.

We have proved that T, the mean total kinetic energy of a molecule, is equal to $\frac{m\tau}{3}$, where m is the number of degrees of freedom of the molecule;

$$\therefore \quad \delta Q = N\left(\frac{m}{3} + \frac{d\chi}{dt}\right)\delta\tau.$$

Next let the volume be allowed to increase so that the pressure remains constant, and let $\delta' Q$ be the heat required to raise the unit of mass from τ to $\tau+\delta\tau$ in this case.

Since external work is performed equal to $p\,\delta v$ we must have in this case

$$\delta' Q = N\left(\frac{m}{3} + \frac{d\chi}{dt}\right)\delta\tau + p\,\delta v.$$

But we know that $pv = \frac{2N}{3}\cdot\tau$, and since p remains constant it follows that

$$p\,\delta v = \frac{2N}{3}\,\delta\tau;$$

$$\therefore \quad \frac{\delta' Q}{\delta Q} = \frac{m + 3\frac{d\chi}{dt} + 2}{m + 3\frac{d\chi}{dt}}.$$

All that we know of $\frac{d\chi}{dt}$ is that it must necessarily be positive, and of m that it must be integral and not less than 3; writing therefore e for $3\frac{d\chi}{dt}$ in the calculated value of the ratio of the specific heats, this becomes

$$\frac{m+e+2}{m+e},$$

or

$$1+\frac{2}{m+e}.$$

There is one gas* for which the ratio is $1\frac{2}{3}$ very approximately, giving us therefore $m+e=3$, and thus agreeing with the case of elastic spheres, where there are three degrees of freedom, determined by the coordinates of the centre, so that $m=3$ and $e=0$.

For the majority of observed gases, however, the ratio is 1·408, giving us

$$\frac{2}{m+e}=\cdot 408,$$

and

$$m+e=4\cdot 9.$$

For a few gases the ratio is 1·3, whence we get

$$\frac{2}{m+e}=\cdot 3,$$

and

$$m+e=6\cdot\dot{6}.$$

And for a few other gases the ratio falls as low as 1·26, giving us

$$m+e=8, \text{ nearly.}$$

* Mercury gas, for which the ratio in question has been determined at 1.67.

One great difficulty in the establishment of the kinetic theory of gases is to conceive a molecule so constituted as to give a suitable positive and integral value for m in the cases we have mentioned, especially for that most general case of all in which

$$m + e = 4{\cdot}9.$$

There is also a further difficulty arising from the following considerations.

It is known that the light emitted by heated gas, so long as the gas is of no great density, consists of rays of one or more definite kinds of refrangibility, so that when this light is examined by the spectroscope, the spectrum produced consists of one or more bright lines, narrow and distinct, the intervening spaces being dark. As the density of the gas increases, these bright lines become broader and the intervening spaces more luminous, until, as the gas becomes very much condensed, a continuous spectrum is produced.

If we conceive our gas to be represented by a number of moving molecules, as in the hypothesis now under consideration, the motion of translation or agitation of these *molecules* is exceedingly irregular, the intervals between successive encounters and the velocities of a molecule during successive free paths not being subject to any law. It will be different however with the internal motions or vibrations of each molecule. When there is a long free path very many such vibrations may take place in the interval between successive encounters. At each encounter the whole molecule is roughly shaken. During the free path it vibrates according to its own laws, and these vibrations, as is the case in every connected system, may be resolved into a number of simple vibrations, the law of each of which is that of the simple pendulum. At any instant the

number of molecules in collision is negligible in comparison with the whole number of molecules in the region under consideration. And therefore at any instant we have a collection of a very great number of bodies, all of which may be regarded as performing precisely the same set of vibrations. If these molecules be capable of communicating their vibrations to the luminiferous ether, the result will be light of one or more definite kinds of refrangibility, provided there be any light at all—that is, provided that the vibrations be of such a period as to belong to the luminous part of the spectrum. As the density of this medium is increased, the length of the free path of each molecule is diminished, and since each fresh encounter disturbs the regularity of the series of vibrations, we must no longer regard the whole of the bodies or molecules, but only a large majority of them at any instant, as performing the same sets of vibrations; the result therefore will be light of one or more definite kinds of refrangibility, with a mixture of fainter light of no definite refrangibility, or, viewed under the spectroscope, bright lines of light, along with a ground of diffused light forming a continuous spectrum.*

In estimating the difficulty presented by these considerations in the way of the establishment of the Kinetic Theory of Gases, it must be borne in mind that they assume a sensibly *instantaneous* return to the permanent state after any disturbance of the medium. In that permanent state, as we have shewn, there is an equal partition of the average kinetic energy among the different degrees of freedom, that is to say, the total kinetic energy is $\frac{m}{3}$ times the kinetic energy of agitation, whence in the case of a perfect

* See Maxwell, 'Theory of Heat,' p. 306.

gas, $p\delta v$ or $dW = \frac{2}{m}\,dT$, where dT is the total increase of kinetic energy; and therefore the ratio of the specific heats, or $\frac{dT+d\chi+dW}{dT+d\chi}$, becomes, as we have seen,

$$\frac{dT+d\chi+\frac{2}{m}\,dT}{dT+d\chi} = \frac{dT\left(1+\frac{2}{m}\right)+d\chi}{dT+d\chi},$$

$$\text{or} \quad \frac{m+2+e}{m+e},$$

where e is written for the small positive quantity $\frac{d\chi}{dT}$ or $3\frac{d\chi}{d\tau}$, because $\frac{d\chi}{d\tau} = \frac{3}{m}\cdot\frac{d\chi}{d\tau}$.

But the rate at which the medium tends to the ultimate state varies, or may vary, greatly with the nature of the disturbance. For example, it has been shewn above, Art. 15, that in a medium of plane circular disks, in each of which the centre of inertia is at the distance c from the centre of figure, an inequality between the mean kinetic energy corresponding to the rotation and that corresponding to either of the translational velocity components may, if c be small, tend to disappear at an infinitely slower rate than when the disturbance arose from an inequality between the mean kinetic energies corresponding to the translational velocity components themselves. Now it is reasonable to believe that the first effect of such a disturbance of the medium as an increase of heat, or energy, would be shewn in the alteration of the agitation energy of the molecules upon which the temperature depends, and these molecules may be so constituted that the time required before the equal partition of the perma-

nent state is reached may be finite or even large; and during such time the external work δW is bearing to δT the whole increase of kinetic energy a larger ratio than $\frac{2}{m}$; or in other words, the apparent value of γ, the ratio of the specific heat as observed during this interval, would be greater than the value

$$\frac{dT\left(1+\frac{2}{3m}\right)+d\chi}{dT+d\chi},$$

which it would have if the permanent state were reached instantaneously.

In the case of the problem referred to in Art. 15 Professor Tait finds that the difference of the average energies of the two systems of spheres will on certain numerical assumptions fall to ·01 of its original value in $\frac{1}{3}\times 10^{-9}$ of a second, these assumptions being reasonable on the hypothesis of certain gases being represented by a medium composed of such spheres.

The principles involved are such as would lead to a similar result in the investigation of the rate at which an equality would be arrived at in the average kinetic energies corresponding to the three components of agitation of either set of spheres.

Replacing spheres by molecules we may, therefore, conclude that the equalisation of the components of agitation energy in a medium of moving molecules representing a perfect gas takes place, sensibly at least, instantaneously, and it is on the assumption of such instantaneous equalisation among these components that the velocity of transmission of sound waves and other physical properties of the medium is found to agree with experimental results, but it need not necessarily follow that there is this *instantaneous*

equalisation among the energies corresponding to *all* the degrees of freedom, so that it is not necessarily a fatal objection to the theory that a difficulty should exist which is based solely upon the assumption of such universal *instantaneous* equalisation.

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